JOURNAL

OF

THE CHEMICAL SOCIETY.

Committee of Publication:

H. E. Armstrong, Ph.D., F.R.S.
W. Crookes, F.R.S.
F. R. Japp, M.A., Ph.D., F.R.S.
A. K. Miller, Ph.D.
Hugo Müller, Ph.D., F.R.S.
W. H. Perkin, Ph.D., F.R.S.
S. U. Pickering, M.A.
R. T. Plimpton, Ph.D.
W. J. Russell, Ph.D., F.R.S.
J. Millar Thomson, F.R.S.E.
T. E. Thorpe, Ph.D., F.R.S.

Editor:
C. E. Groves, F.R.S.

Sub Editor:
A. J. Greenaway.

Vol. [illegible]

1887. TRANSACTIONS.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1887.

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE

CONTENTS.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

PAGE

I.—On the Synthetical Formation of Closed Carbon-chains. Part II. On some Derivatives of Tetramethylene. By W. H. Perkin, Jun., Ph.D. 1

II.—Preparation and Hydrolysis of Hydrocyanides of the Diketones. By Francis R. Japp, F.R.S., and N. H. J. Miller, Ph.D. 29

III.—Note on some Double Thiosulphates. By J. B. Cohen, Ph.D., Assistant Lecturer, Owens College, Manchester . 38

IV.—On the Action of Silicon Tetrachloride on the Aromatic Amido-compounds. By Arthur Harden, B.Sc., Dalton Chemical Scholar in the Owens College 40

V.—Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide. By Edward Divers and Tamemasa Haga . . . 48

VI.—On Morindin and Morindon. By T. E. Thorpe, F.R.S., and T. H. Greenall 52

VII.—Spectroscopic Notes on the Carbohydrates and Albuminoids from Grain. By W. N. Hartley, F.R.S., Professor of Chemistry, Royal College of Science, Dublin . . . 58

VIII.—The Action of Salicylic Aldehyde on Sodium Succinate in presence of Acetic Anhydride. By Gibson Dyson, Ph.D., Demonstrator of Chemistry, Normal School of Science, South Kensington 61

IX.—Decomposition of Sodium Carbonate by Fusion. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College 72

X.—The Heat of Hydration of Salts. Cadmium Chloride. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College 75

XI.—Contributions from the Laboratory of Gonville and Caius College, Cambridge. No. VIII. On Bismuthates. By M. M. Pattison Muir, M.A., Fellow, and Douglas J. Carnegie, B.A., Scholar, of Gonville and Caius College 77

XII.—Derivatives of Tolylbenzene. By Thomas Carnelley, D.Sc. (Lond.), and Andrew Thomson, M.A., B.Sc. (Edin.), University College, Dundee 87

PAGE

XIII.—The Amount of Chlorine in Rain-water collected at Cirencester. By EDWARD KINCH, Royal Agricultural College, Cirencester 92

XIV.—Some Analogous Phosphates, Arsenates, and Vanadates. By JOHN A. HALL, Student in the Laboratory of Owens College 94

XV.—On some Azines. By FRANCIS R. JAPP, F.R.S., and COSMO INNES BURTON, B.Sc. 98

XVI.—Researches on the Constitution of Azo- and Diazo-derivatives. I. Diazoamido-compounds. By RAPHAEL MELDOLA, F.R.S., Professor of Chemistry, and F. W. STREATFEILD, Demonstrator of Chemistry, in the Finsbury Technical College, City and Guilds of London Institute . 102

XVII.—On the Distribution of the Nitrifying Organism in the Soil. By R. WARINGTON 118

XVIII.—The Influence of Silicon on the Properties of Iron and Steel. Part I. By THOMAS TURNER, Assoc. R.S.M., Lecturer on Metallurgy, Mason College, Birmingham . . 129

XIX.—Isomeric Change in the Phenol Series. I. The Action of Bromine on the Dibromonitrophenols. By ARTHUR R. LING 147

XX.—Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra. Part VIII. A Study of Coloured Substances and Dyes. By W. N. HARTLEY, F.R.S., Professor of Chemistry, Royal College of Science, Dublin . . . 152

XXI.—Some Silicon Compounds and their Derivatives. I. The Action of Silicon Tetrabromide on Thiocarbamide. By J. EMERSON REYNOLDS, M.D., F.R.S., Professor of Chemistry, University of Dublin 202

XXII.—Notes on the recent papers by A. von Baeyer and Julius Thomsen: "On the Constitution of Benzene." By ALEX. K. MILLER, Ph.D. 208

XXIII.—Agricultural Experiments with Iron Sulphate as a Manure during 1886. By A. B. GRIFFITHS, Ph.D., F.R.S.E., Principal and Lecturer on Chemistry, School of Science, Lincoln, late Lecturer on Chemistry, Technical School, Manchester, &c. 215

XXIV.—The Action of Triphenylmethyl Bromide on Ethylic Sodiomalonate. By G. G. HENDERSON, M.A., B.Sc., Assistant to the Professor of Chemistry, University of Glasgow 224

XXV.—The Synthetical Formation of Closed Carbon-chains. Part II, continued. Some Derivatives of Tetramethylene. By H. G. COLMAN, B.Sc., and W. H. PERKIN, Jun., Ph.D. . 228

PAGE

XXVI.—The Synthetical Formation of Closed Carbon-chains. Part III. Some Derivatives of Pentamethylene. By W. H. Perkin, Jun., Ph.D. 240

XXVII.—Absorption of Gases by Carbon. By Charles J. Baker, B.A., Demonstrator of Chemistry, University Museum, Oxford. 249

XXVIII.—An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds. By Henry E. Armstrong, F.R.S. 258

XXIX.—The Action of Chlorine on Organic Thiocyanates. Part I. Methyl Thiocyanate. By J. William James, Ph.D., University College of South Wales, Cardiff . . 268

XXX.—The Decomposition of Potassium Chlorate and Perchlorate by Heat. By Percy F. Frankland, Ph.D., B.Sc., A.R.S.M., and John Dingwall 274

XXXI.—Potassium Chlorate and Perchlorate. By Frank L. Teed, D.Sc. 283

XXXII.—On the Formation of Ethylic Cyanacetoacetate. By J. William James, Ph.D., F.C.S., University College of South Wales, Cardiff 287

XXXIII.—The Influence of Temperature on the Heat of Dissolution of Salts. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College . . 290

XXXIV.—Contributions from the Laboratory of Gonville and Caius College, Cambridge. No. IX. Periodates. By C. W. Kimmins, D.Sc., B.A., late Scholar of Downing College, Cambridge 356

XXXV.—On Tartaric and Racemic Acids, and the Magnetic Rotation of their Ethereal Salts. By W. H. Perkin, Ph.D., F.R.S. 362

XXXVI.—The Colouring Matter of *Drosera Whittakeri.* By Edward H. Rennie, M.A., D.Sc., Professor of Chemistry in the University of Adelaide, South Australia . . . 371

XXXVII.—Further Notes on the Di-Haloïd Derivatives of Thiocarbamide. By George McGowan, Ph.D., Demonstrator of Chemistry, University College of North Wales, Bangor 378

XXXVIII.—Researches on Chrom-organic Acids. By Emil A. Werner, Assistant in the Chemical Laboratory, University of Dublin 383

XXXIX.—Supersaturation of Salt Solutions. By W. W. J. Nicol, M.A., D.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham 389

XL.—Action of Heat on Peroxide of Nitrogen. By Arthur

PAGE

Richardson, Ph.D., Assistant Lecturer, University College, Bristol 397

XLI.—Formation of Pyridine-derivatives from Citric Acid, and on the Constitution of Pyridine. By Dr. S. Ruhemann, Jacksonian Demonstrator in the University of Cambridge. 403

XLII.—On Silver containing Bismuth. By William Gowland, Associate of the Royal School of Mines, Chemist and Assayer of the Imperial Mint, Osaka, Japan, and Yoshimasa Koga, Assistant Assayer 410

XLIII.—Suboxide of Silver, Ag_4O. By G. H. Bailey, D.Sc., Ph.D., and G. J. Fowler, B.Sc., the Owens College . . 416

XLIV.—Anhydracetonebenzil. By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc. 420

XLV.—Condensation Compounds of Benzil with Ketones. By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc. . 431

XLVI.—Researches on the Constitution of Azo- and Diazo-derivatives. II. Diazo-amido-compounds (*continued*). By Raphael Meldola, F.R.S., Professor of Chemistry, and F. W. Streatfeild, Demonstrator of Chemistry in the Finsbury Technical College, City and Guilds of London Institute 434

Annual General Meeting 452

XLVII.—Dehydracetic Acid. By W. H. Perkin, Jun., Ph.D. . 484

XLVIII.—A Contribution to the Study of Well Waters. By Robert Warington, F.R.S. 500

XLIX.—Constitution of Glycosine. By Francis R. Japp, F.R.S., and E. Cleminshaw, M.A. 552

L.—Diphenylglyoxaline and Methyldiphenylglyoxaline. By Francis R. Japp, F.R.S. 557

LI.—On the Atomic Weight of Gold. By T. E. Thorpe, F.R.S., and A. P. Laurie, B.Sc., F.R.S.E. 565

LII.—On the Atomic Weight of Silicon. By T. E. Thorpe, F.R.S., and J. W. Young, B.A. 576

LIII.—Note on Substitution in the Benzene Nucleus. By F. H. Morley, M.A. 579

LIV.—An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds. (Second Notice.) By Henry E. Armstrong, F.R.S. 583

LV.—Researches on Silicon Compounds and their Derivatives. II. A New Chlorobromide of Silicon. By J. Emerson Reynolds, M.D., F.R.S., Professor of Chemistry, University of Dublin 590

PAGE

LVI.—On the Thermal Phenomena of Neutralisation, and their bearing on the Nature of Solution and the Theory of Residual Affinity. By SPENCER UMFREVILLE PICKERING, M.A., Professor of Chemistry at Bedford College . . . 593

LVII.—Crystals in Basic Converter Slag. By J. E. STEAD and C. H. RIDSDALE, and Crystals from the Basic Slag. By H. A. MIERS, M.A., F.G.S. 601

LVIII.—Ozone from Pure Oxygen: its Production and its Action on Mercury, with a Note on the Silent Discharge of Electricity. By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College, and J. TUDOR CUNDALL . . . 610

LIX.—The Volumetric Relations of Ozone and Oxygen. A Lecture Experiment. By W. A. SHENSTONE and J. TUDOR CUNDALL 625

LX.—The Action of Metallic Alkylates on Mixtures of Ethereal Salts with Alcohols. By T. PURDIE, Ph.D., B.Sc., Professor of Chemistry in the University of St. Andrews . . 627

LXI.—On Phlorizin. By EDWARD H. RENNIE, M A., D.Sc., Professor of Chemistry in the University of Adelaide, South Australia 634

LXII.—Further Notes on the Chemical Action of *Bacterium aceti*. By ADRIAN J. BROWN 638

LXIII.—The Composition of Prussian Blue and Turnbull's Blue. By EDGAR J. REYNOLDS 644

LXIV.—On the Formation of Hyponitrites. By WYNDHAM R. DUNSTAN, Professor of Chemistry to the Pharmaceutical Society, and T. S. DYMOND 646

LXV.—The Relation between Sulphites and Nitrites of Metals other than Potassium. By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, F.C.S., Imperial University, Tôkyô, Japan 659

LXVI.—Anacardic Acid. By Dr. S. RUHEMANN and S. SKINNER 663

LXVII.—Sulphinic Compounds of Carbamide and Thiocarbamide. By GEORGE MCGOWAN, University College of North Wales, Bangor 666

LXVIII.—Note on a New Class of Voltaic Combinations in which Oxidisable Metals are replaced by Alterable Solutions. By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry, and C. THOMPSON, Demonstrator of Chemistry, in St. Mary's Hospital Medical School 672

LXIX.—The Determination of Atomic Weights by means of the Normal Sulphate. By G. H. BAILEY, D.Sc. . . . 676

LXX.—The Action of Acetyl Chloride on Acetoximes. By VICTOR MEYER and ARTHUR W. WARRINGTON, B.Sc. . . 683

PAGE

LXXI.—Note on an Improved Form of Apparatus for the Separation of Iodine, Bromine, and Chlorine. By M. DECHAN, F.C.S. 690

LXXII.—Notes on Anhydro-bases. I. Ethenyltriamidonaphthalene. By RAPHAEL MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C. 691

LXXIII.—Dibenzyl Ether. By C. W. LOWE, Student in the Owens College 700

LXXIV.—The Synthetical Formation of Closed Carbon-chains. Part II (*continued*). On the Action of Trimethylene Bromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate, and Acetonedicarboxylate. By W. H. PERKIN, Jun., Ph.D. . 702

LXXV.—On Aluminium in the Ashes of Flowering Plants. By HIKOROKURO YOSHIDA, F.C.S., Assistant Professor of Chemistry, College of Science, Imperial University, Tokyo, Japan 748

LXXVI.—Some Ethereal Salts of the Vanadium Acids. By JOHN A. HALL, Owens College 751

LXXVII.—Evaporation and Dissociation. Part VII. A Study of the Thermal Properties of a Mixture of Ethyl Alcohol and Ethyl Oxide. By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc. 755

LXXVIII.—The Compounds of Ethyl Alcohol with Water. By D. MENDELÉEFF 778

LXXIX.—Isomeric Change in the Phenol Series. (Second Notice.) By ARTHUR R. LING 782

LXXX.—The Effects of Dilution and the Presence of Sodium Salts and Carbonic Acid upon the Titration of Hydroxylamine by Iodine. By TAMEMASA HAGA 794

LXXXI.—The Action of Light on the Hydrides of the Halogens in Presence of Oxygen. By ARTHUR RICHARDSON, Ph.D., Lecturer on Chemistry, University College, Bristol . . 801

LXXXII.—Note on the Influence of Liquid Water in promoting the Interaction of Hydrogen Chloride and Oxygen on Exposure to Light. By HENRY E. ARMSTRONG, F.R.S. . 806

LXXXIII.—On the Magnetic Rotation and Densities of Chloral, Chloral Hydrate, and Hydrated Aldehydes. By W. H. PERKIN, Ph.D., F.R.S. 808

LXXXIV.—The Synthetical Formation of Closed Carbon-Chains. Part I (*continued*). The Action of Ethylene Bromide on the Sodium-derivatives of Ethylic Acetoacetate, Benzoylacetate, and Acetonedicarboxylate. By P. C. FREER, Ph.D., and W. H. PERKIN, Jun., Ph.D. 820

PAGE

LXXXV.—The Synthetical Formation of Closed Carbon-chains. Part I (*continued*). Trimethylenedicarboxylic Acid. By W. H. Perkin, Jun., Ph.D. 849

LXXXVI.—Experiments for the purpose of comparing the Equivalent of Zinc with that of Hydrogen. By Lieut.-Colonel H. C. Reynolds, late R.E., and Prof. W. Ramsay, Ph.D. 854

LXXXVII.—Note on the Atomic Weight of Gold. By T. E. Thorpe and A. P. Laurie, Esq., B.A. 866

LXXXVIII.—Certain Products from Teak. Preliminary Notices. By R. Romanis, D.Sc., F.C.S., Rangoon College . 868

JOURNAL

OF

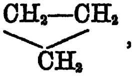
THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

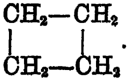
I.—*The Synthetical Formation of Closed Carbon-chains.* Part II. *On some Derivatives of Tetramethylene.*

By W. H. Perkin, Jun., Ph.D.

In Part I of this paper, which I had the honour of laying before the Society last year (Trans., 1885, 801), I gave a short description of some derivatives of trimethylene,



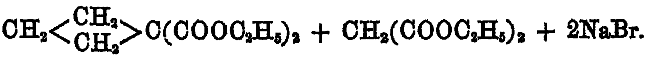
and I now desire to communicate to the Society the results of my experiments on the synthetical formation of compounds containing the tetramethylene-ring,



These derivatives may be easily obtained by reactions exactly similar to those employed for the formation of trimethylene-derivatives.

Thus, ethylic malonate when treated with sodic ethylate and trimethylene bromide is converted into the ethereal salt of tetramethylenedicarboxylic acid [1, 1]*—

$$2CHNa(COOC_2H_5)_2 + CH_2Br{\cdot}CH_2{\cdot}CH_2Br =$$



$$CH_2{<}{\scriptstyle CH_2 \atop CH_2}{>}C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 + 2NaBr.$$

If, however, ethylic acetoacetate be substituted for ethylic malonate in the above reaction, a different series of compounds is formed, a description of which must be reserved for a future paper.

---

* With regard to the nomenclature of these ring-bodies, see Part I of this paper (Trans., 1886, 806).

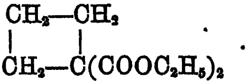
This paper has, for convenience sake, been divided into the following chapters:—

I. Preparation and properties of tetramethylenedicarboxylic acid (1, 1), tetramethylenemonocarboxylic acid, and their ethereal salts.

II. Tetramethylenetetracarboxylic acid (1, 1, 2, 2), and tetramethylenedicarboxylic acid (1, 2).

III. Diacetyltetramethylenedicarboxylic acid (1, 1, 2, 2).

I. *Ethylic Tetramethylenedicarboxylate* (1, 1),



$$\begin{array}{ll} \mathrm{CH_2{-}CH_2} & \\ | \quad\;\;\; | & \\ \mathrm{CH_2{-}C(COOC_2H_5)_2} & . \end{array}$$

In order to prepare this ethereal salt, the following method, which I give in full, has usually been employed.

14·5 grams of sodium are dissolved in about 160 grams of absolute alcohol, and when thoroughly cold a mixture of 100 grams of ethylic malonate and 64 grams of trimethylene bromide is slowly poured in, the whole being well shaken and cooled during the operation. During the mixing, the sodium compound of ethylic malonate generally separates out as a white gelatinous mass, but this soon disappears, especially on warming, a clear liquid being formed. On allowing this to stand, sodic bromide is precipitated, and the temperature gradually rises, the reaction in most cases being so violent as to cause the alcohol to boil; as soon as it has cooled down, the decomposition is generally at an end. In order to test this, a small quantity is taken out, diluted with a little water, and tested with litmus-paper, when it should have a perfectly neutral reaction.

If, however, it should still be alkaline, it is gently warmed on a water-bath till the reaction is complete.

In order to isolate the product, the whole is dissolved in about 2—3 times its bulk of water, and extracted two or three times with ether.* On distilling off the ether, a colourless oil remains, which is next roughly purified by distillation with steam; by this means all the ethylic tetramethylenedicarboxylate and regenerated ethylic malonate are driven over, a thick oil consisting principally of ethylic pentanetetracarboxylate remaining in the retort.

The distillate is then extracted twice or thrice with ether, the ethereal solution washed, once with water and once with dilute carbonate of soda solution, and dried over calcic chloride. On distilling off the ether, about 110 grams of a colourless oil are left, which is further purified by fractional distillation. Below 175°, a small quantity of unchanged trimethylene bromide passes over, then the temperature rises rapidly to 190°, between which and 240° about 60 grams of oil, consisting of a mixture of ethylic malonate and tetramethylenedicarboxylate distils over.

---

* Saturating with common salt, before extracting with ether, has been found very advantageous.

In order to separate these ethereal salts, it is necessary to fraction repeatedly and carefully with a reflux apparatus. In this way 26—28 grams of nearly pure ethylic tetramethylenecarboxylate may be obtained, boiling between 218° and 223° (720 mm.). When operating with larger quantities, a yield of about 30—34 grams has been obtained from every 100 grams ethylic malonate. Varying the proportions of the different ingredients in this reaction does not appear to affect the yield very much.

The following three experiments were tried in order to determine this:—

Used.	I.	II.	III.	Yield, p.c.	
Ethylic malonate......	2 mol.	1 mol.	1 mol.	I....	30
Trimethylene bromide .	1 „	2 „	1 „	II....	33
Sodium..............	2 „	1 „	2 „	III....	28

Pure ethylic tetramethylenedicarboxylate boils at 220—221° (720 mm.).

The following numbers were obtained on analysis:—

I. 0·2200 gram substance gave 0·4799 gram CO_2 and 0·1605 gram H_2O.

II. 0·1618 gram substance gave 0·3561 gram CO_2 and 0·1170 gram H_2O.

	Found.		Theory.
	I.	II.	$C_3H_6 \colon C(COOC_2H_5)_2$.
C......	59·50	60·03 per cent.	60·00 per cent.
H	8·10	8·04 „	8·00 „
O......	32·40	31·93 „	32·00 „

Ethylic tetramethylenedicarboxylate is a colourless mobile liquid having a slight odour of camphor. It is not acted on by bromine at ordinary temperatures, but on boiling, the colour of the bromine disappears, torrents of hydrogen bromide being given off.

The density and magnetic rotation determinations of this compound, which were carried out by my father, gave the following results:—

$$d\frac{9^\circ}{9^\circ} = 1{\cdot}05328.$$

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}04817.$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}04051.$$

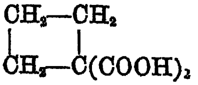
Magnetic Rotations.

t	Sp. rotation.	Mol rotation.
20·3	0·9320	9·921
20·1	0·9337	9·939
19·9	0·9374	9·977
19·6	0·9348	9·946
17·6	0·9372	9·955
17·6	0·9336	9·918
17·6	0·9341	9·922
Average 18·9	0·9346	9·940

Dr. Gladstone was so kind as to determine the refractive equivalent, and gave me the following account of his results:—

t	Sp gr.	μ_{A}.	μ_{D}	μ_{H}
2[illegible]	1·0383	1·4353	1·4330	1·4477

Observed.		Normal calculated.	
Ref eq. A.	Disp eq H – A	Ref. eq. A.	Disp eq H – A.
82·46	3·76	83·2	3·78

Tetramethylenedicarboxylic Acid (1, 1), 

$$\begin{array}{l}CH_2—CH_2\\ |\qquad\quad |\\ CH_2—C(COOH)_2\end{array}$$

The following method was employed to hydrolyse ethylic tetramethylenedicarboxylate so as to obtain the free acid:—

80 grams of the nearly pure ethereal salt was dissolved in an equal bulk of alcohol and a moderately strong solution of alcoholic potash (containing 50—60 grams KOH) then run in slowly. Hydrolysis sets in immediately, the mass often becoming so hot as to cause the alcohol to boil. As soon as the violence of the reaction has subsided, the whole is heated on a water-bath for five hours, and evaporated almost to dryness. The residue is next dissolved in water, and again evaporated in order to entirely remove the alcohol; the solution of the residual potassic salt in a little water, is then acidified with dilute sulphuric acid, and repeatedly (at least 10 times) extracted with pure

ether. The ethereal solution, after being dried over calcic chloride, is evaporated, when the new acid is left as a beautiful colourless crystalline cake. These crystals, which sometimes contain a trace of oily matter, are roughly purified by spreading them out on a porous plate, and are afterwards dissolved in a little warm ether. If this ethereal solution is allowed to evaporate spontaneously, beautifully transparent crystals of tetramethylenedicarboxylic acid soon separate, and are easily obtained pure by one recrystallisation.

The following results were obtained on analysis:—

I. 0·2307 gram substance gave 0·4225 gram CO_2 and 0·1226 gram H_2O.

II. 0·1238 gram substance gave 0·2276 gram CO_2 and 0·0659 gram H_2O.

	Found.			Theory.
	I.	II.		$C_3H_6 : C(COOH)_2$.
C	49·95	50·13	per cent.	50·00 per cent.
H	5·90	5·91	,,	5·56 ,,
O	44·15	43·96	,,	44·44 ,,

When pretty quickly heated, tetramethylenedicarboxylic acid (1, 1) melts at 154—156°; if slowly heated, however, it decomposes at a lower temperature, carbonic anhydride being given off.

It is easily soluble in water, moderately easily in ether, chloroform, and benzene, but only sparingly in light petroleum. The aqueous solution, when evaporated over sulphuric acid in a vacuum, deposits the acid in thick prisms, but the most beautiful crystals are obtained when a considerable quantity of a strong ethereal solution is allowed to evaporate spontaneously.

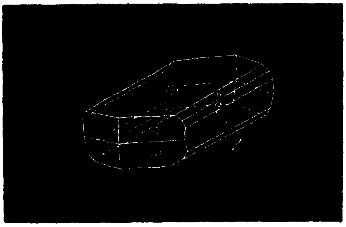
Professor Haushofer was kind enough to measure some of these crystals for me, and gave the following account of them:—

Tetramethylenedicarboxylic Acid.

Crystalline System. Monoclinic.

$$a : b : c = 1·0324 : 1 : 1·1354.$$

$$\beta = 88° 58'.$$



Tabular crystals of the combination—

$0P = (001) = c$
$-7P = (771) = o$
$7P = (77\bar{1}) = w$
$\infty\bar{P}\infty = (010) = b$
$\bar{P}\infty = (011) = q$
$\frac{1}{2}\bar{P}\infty = (012) = n$

Cleavage perfectly conformable to the plane of symmetry *b*; on the plane *b*, the direction of extinction (with crossed Nicols) forms an angle of 38° with the edge *b c*.

	Measured.		Calculated.	
$c : o = (001)(771) =$	*95°	54	—	—
$c : w = (00\bar{1})(77\bar{1}) =$	94	32	94°	28′
$o : o = (771)(7\bar{7}1) =$	*88	48	—	—
$w : w = (77\bar{1})(7\bar{7}\bar{1}) =$	88	32	—	—
$c : n = (001)(012) =$	150	12	150	25
$c : q = (001)(011) =$	131	20	131	23

The solution of tetramethylenedicarboxylic acid in chloroform does not appear to be affected by bromine, even after standing for weeks, neither does hydrobromic acid act on the acid. Nearly the whole of the acid was recovered from a solution of it in concentrated hydrobromic acid (sp. gr. 1·83) which had been standing for six weeks, on shaking it up with ether. This is somewhat striking when it is remembered how easily trimethylenedicarboxylic acid is acted on by hydrobromic acid (Part I, page 814).

Salts of Tetramethylenedicarboxylic Acid (1, 1).

Ammonium Salt.—This salt was prepared by dissolving the acid in a slight excess of ammonia and allowing the solution to evaporate over sulphuric acid in a vacuum. It crystallises in long colourless needles, and is very easily soluble in water.

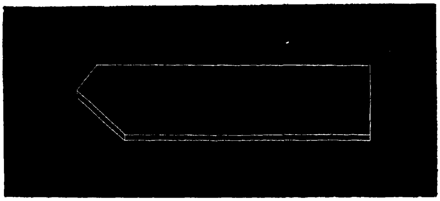
Silver Salt.—If nitrate of silver is added to a neutral solution of the ammonium salt, a soluble acid silver salt is at first produced, but on adding excess a white precipitate of the neutral salt is thrown down.

This salt, after being well washed and dried, gave the following results on analysis:—

I. 0·2595 gram substance gave 0·1904 gram CO_2 and 0·0451 gram H_2O.
II. 0·2265 gram substance gave 0·1359 gram silver.

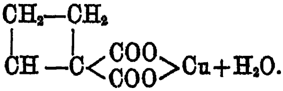
	Found.	Theory. $C_3H_6 : C(COOAg)_2$.
C......	20·02 per cent.	20·11 per cent.
H......	1·94 „	1·68 „
Ag	60·00 „	60·33 „
O......	18·04 „	17·88 „

Copper Salt.—The addition of cupric sulphate to a fairly concentrated solution of the ammonium salt produces a beautiful deep-blue solution but no precipitate. If, however, this solution is warmed on a water-bath, the copper salt soon crystallises out in magnificent blue needles, which when examined under the microscope are observed to have the form—



These crystals, which probably belong to the monosymmetric system, show a most beautiful play of colours when seen by polarised light.

The copper salt appears to have the formula—



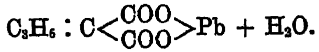
$$\begin{array}{l} CH_2—CH_2 \\ \;| \qquad\;\; | \\ CH\;—C\!<\!\begin{matrix}COO\\COO\end{matrix}\!>\!Cu + H_2O. \end{array}$$

Analysis.

I. (α) 0·2085 gram substance (dried over sulphuric acid) lost on heating to 150° 0·0150 gram.
(β) 0·1935 gram substance gave 0·1749 gram CuO.
II. 0·2640 gram substance (dried at 150°) gave 0·1010 gram CuO.
III. 0·1693 gram substance (dried over sulphuric acid) gave 0·0601 gram CuO.

	Found.				Theory.	Theory.
	I.	II.	II.		$C_6H_6O_4Cu$.	$C_6H_6O_4Cu + H_2O$.
Cu..	30·90	30·54	28·30	per cent.	30·83	28·30
H_2O_2	7·19	—	—	„	—	8·06

Lead Salt.—If plumbic acetate is added to a dilute solution of ammonic tetramethylenedicarboxylate, a white amorphous precipitate is thrown down which becomes crystalline on vigorous shaking. After filtering off, well washing with water and drying over sulphuric acid in a vacuum, this salt has the formula



$$C_3H_6 : C{<}{\begin{smallmatrix}COO\\COO\end{smallmatrix}}{>}Pb + H_2O.$$

Analyses.

I. 0·2324 gram substance lost on heating to 150°, 0·0127 gram; thus dried, the substance gave on heating with sulphuric acid, 0·1903 gram $PbSO_4$.

II. 0·2557 gram substance (dried at 140°) gave 0 2222 gram $PbSO_4$.

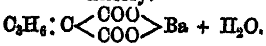
	Found.		Theory.	Theory.
	I.	II.	$C_6H_6O_4Pb$.	$C_6H_6O_4Pb+H_2O$.
Pb ..	59·18	59·37 p. c.	59·31 p. c.	—
H_2O ..	5·46	—	—	4·90 p. c.

This lead salt is almost insoluble in cold water, and very sparingly soluble in hot water.

If the hot concentrated solution is allowed to cool, the salt crystallises out in four-sided prisms.

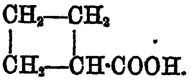
Barium Salt.—If baryta-water is added to the solution of tetramethylenedicarboxylic acid in water, no precipitate is formed at first, but on adding excess a white apparently amorphous precipitate is thrown down which is the neutral barium salt of the acid. After being well washed, and dried over sulphuric acid, it gave the following results on analysis :—

0·4002 gram substance lost on heating at 150—160°, 0·0232 gram, and gave on treating with sulphuric acid, 0·3117 gram $BaSO_4$.

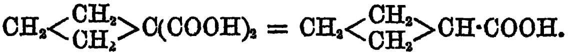
	Found.	Theory.  $C_3H_6 : C{<}{\begin{smallmatrix}COO\\COO\end{smallmatrix}}{>}Ba + H_2O$.
Ba......	45·82 per cent.	46·12 per cent.
H_2O	5·77 „	6 06 „

This salt, when examined under the microscope, is found not to be amorphous, but to consist of a mass of slender needles. It is sparingly soluble in water.

Tetramethylenemonocarboxylic Acid,



When tetramethylenedicarboxylic acid [1, 1] is heated to a few degrees above its melting point, it is rapidly decomposed with evolution of carbonic anhydride and formation of tetramethylenemonocarboxylic acid, according to the equation—



$$CH_2<{CH_2 \atop CH_2}>C(COOH)_2 = CH_2<{CH_2 \atop CH_2}>CH\cdot COOH.$$

In order to effect this decomposition, the dicarboxylic acid is heated in a small Würtz flask at 210—220°. As soon as the acid has melted, carbonic anhydride begins to be evolved and a colourless oil distils over, very little residue remaining in the retort. The distillate when fractioned comes over almost entirely between 188° and 193° (if the dicarboxylic acid was pure), and on refractioning this once or twice the new acid is easily obtained pure as a colourless oil boiling constantly at 191° (720 mm.).

The analyses gave the following numbers :—

I. 0·1846 gram substance gave 0·4082 gram CO_2 and 0·1361 gram H_2O.

II. 0·2260 gram substance gave 0·4950 gram CO_2 and 0·1691 gram H_2O.

III. 0·1376 gram substance gave 0·3026 gram CO_2 and 0·0991 gram H_2O.

	Found.				Theory.	
	I.	II.	III.		$C_3H_6 : CH\cdot COOH$.	
C....	60·30	59·74	59·97	per cent.	60·00	per cent.
H ...	8·19	8·31	8·00	„	8·00	„
O ...	31·51	31·95	32·03	„	32·00	„

Tetramethylenemonocarboxylic acid is a colourless oil, of penetrating and very disagreeable odour, somewhat resembling that of butyric acid. It does not solidify when cooled down to 0°. It is sparingly soluble in water, but mixes in all proportions with alcohol, ether, &c. It is easily oxidised when treated with permanganate of potash in alkaline solution, oxalic acid being formed.

Tetramethylenemonocarboxylic acid is not acted on by bromine at ordinary temperatures. The difficulty with which it is attacked by this reagent is very remarkable. On submitting a mixture of 5 grams of acid, 8 grams of bromine, and 20 grams of chloroform to direct sunlight in a sealed tube for 18 days, no apparent change had taken place, and on opening the tube only the slightest trace of hydrobromic acid could be detected. The tube was then sealed up again and heated at 100° for two hours ; even after this treatment, only a very small quantity of hydrobromic acid had been formed. After heating for five hours at 150°, however, the colour of the bromine had entirely disappeared, a colourless liquid being formed, and on opening the tube torrents of hydrogen bromide were evolved. The product when evaporated deposits a heavy brominated acid, the examination of which I am still engaged on.

Tetramethylenemonocarboxylic acid is isomeric with angelic acid, methylcrotonic acid, allylacetic acid, dimethylacrylic acid, and several other unsaturated acids.

Only two salts of tetramethylenemonocarboxylic acid have been examined, namely, the silver and calcium salts.

The *silver salt* is easily obtained by adding nitrate of silver to a neutral solution of the ammonium salt as a heavy white precipitate sparingly soluble in water.

Anaylsis.

0·2579 gram substance gave 0·2740 gram CO_2, 0 0804 gram H_2O, and 0·1348 gram Ag.

	Found.	Theory. $C_5H_7AgO_2$.
C	28·98 per cent.	28 98 per cent.
H	3·46 „	3·38 „
Ag	52·23 „	52·17 „
O	15·33 „	15 47 „

The *calcium* salt of the acid is prepared by boiling the acid with calcic carbonate and water, filtering, and concentrating the filtrate on a water-bath till it becomes of a syrupy consistency. On standing, this deposits the salt in long silky needles, which are very soluble in water.

After recrystallising and allowing to dry by exposure to air for four or five days, this substance was found to have the formula—

$$C_{10}H_{14}O_4Ca + 5H_2O.$$

Analyses.

I. 0·3288 gram dried at 150° for half an hour lost 0·0889 gram.
II. 0·4473 „ „ 120 „ „ 0·0922 „
III. 0·3195 „ treated with sulphuric acid gave 0·1277 gram $CaSO_4$.

	Found.			Theory.
	I.	II.	III.	$C_{10}H_{11}O_4Ca + 5H_2O$.
Ca	—	—	11·75 p. c.	12·19 p. c.
H_2O	27·04	27·09	— „	27·48 „

This salt slowly loses some of its water of crystallisation when exposed to the air for a long time. A sample which had been thus exposed for three weeks, was found to contain 24·59 per cent. H_2O.

Placed over sulphuric acid in a vacuum, it loses all of its water of crystallisation in seven days.

Two analyses of this salt dried at 150°, gave the following results:—

I. 0·3349 gram substance gave 0·1922 gram $CaSO_4$.
II. 0·3208 gram substance gave 0·1830 gram $CaSO_4$.

	Found.		Theory.
	I.	II.	$(C_3H_6 : CH{\cdot}COO)_2Ca$.
Ca......	16·88	16·82 per cent.	16·80 per cent.

On distilling this salt with lime, a gas is given off, which, however, does not appear to be tetramethylene. I hope in a short time to be able to obtain this gas in sufficient quantity for analysis and examination.

Tetramethylenecarboxylic acid, being one of the most simply constituted of the ring compounds yet obtained, it was thought that interesting results might be obtained from the study of its physical properties. The results of the sp. gr. and magnetic rotation determinations, which were performed by my father, are the following:—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}05480,$$

$$d\frac{20^\circ}{20^\circ} = 1{\cdot}05116,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}04761.$$

Magnetic Rotations.

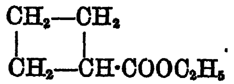
t.	Sp. rotation.	Mol. rotation.
18	0·9561	5·046
18	0·9586	5·059
18	0·9548	5·039
Averages 18	0·9565	5·048

I submitted a very pure sample of this acid to Dr. Gladstone, who was kind enough to examine it optically. The following are the results of his experiments:—

t.	Sp. gr.	μ_A.	μ_D.	μ_H.
25·5	1·046	1·4351	1·4403	1·4561

Observed		Normal calculated.	
Ref. eq. A.	Disp. eq. H – A.	Ref. eq. A.	Disp. eq H – A.
41·60	2·00	41·6	1·89

Ethylic Tetramethylenemonocarboxylate,



This ethereal salt was prepared as follows:—20 grams of the dry silver salt of tetramethylenemonocarboxylic acid was mixed with 25 grams of ethyl iodide and 50 grams of pure ether, and heated on a water-bath for about two hours. At the end of this time, all the silver salt was decomposed, iodide of silver being precipitated. This was removed by filtering, and once or twice extracted with ether.

On carefully distilling off the ether, a colourless oil remained behind, which on the first distillation went over between 148° and 155°; by repeated fractioning, the ethereal salt was easily obtained pure, boiling at 151—151·5° (720 mm.). Analyses:—

I. 0·1450 gram substance gave 0 1193 gram H_2O and 0·3478 gram CO_2.

II. 0·1410 gram substance gave 0·1210 gram H_2O and 0·3390 gram CO_2.

	Found.		Theory.
	I.	II.	$C_3H_6 \colon CH{\cdot}COOC_2H_5$.
C	65·41	65·57 per cent.	65·62 per cent.
H	9·14	9·53 ,,	9 38 ,,
O	25·45	24·90 ,,	25·00 ,,

Ethylic tetramethylenemonocarboxylate is a limpid liquid, of agreeable odour; it does not solidify at 0°.

Trimethylene Iodide, $CH_2I{\cdot}CH_2{\cdot}CH_2I$.

During the course of these experiments, it was thought that if in place of trimethylene bromide a compound were employed capable of reacting more energetically, such as trimethylene iodide, that a better yield of ethylic tetramethylenedicarboxylate would be obtained.

In order to test this, it was first necessary to find some simple method for preparing trimethylene iodide; after several experiments, it was observed that trimethylene bromide is almost quantitatively converted into the corresponding iodide by simply digesting it with alcoholic potassic iodide; thus:—

$$CH_2Br{\cdot}CH_2{\cdot}CH_2Br + 2KI = CH_2I{\cdot}CH_2{\cdot}CH_2I + 2KBr.$$

In preparing the iodide, 50 grams of pure trimethylene bromide are heated on a water-bath with 100 grams of alcohol and 90—100 grams of finely powdered potassic iodide for about an hour. After boiling for a few minutes, potassic bromide begins to be deposited, and at the end of the reaction the mass becomes almost solid; water is now added, and the heavy oil which separates is extracted once or twice with ether. The ethereal solution, which is generally of a brownish colour, is then well washed with water to dissolve out potassic iodide and alcohol, dried over calcic chloride, and freed from iodine by shaking with a small quantity of mercury. On distilling off the ether, nearly pure trimethylene iodide remains. In order to obtain a perfectly pure product, the oil thus obtained is next fractioned under diminished pressure (250 mm); on the first distillation, almost the whole of it passes over between 175° and 183° as a heavy oil of peculiar odour, which, if discoloured by iodine, is again treated with a little mercury and refractioned. Pure trimethylene iodide is a colourless oil boiling at 179° (250 mm.). An analysis gave the following numbers:—

0·3048 gram substance gave 0·4820 gram AgI.

	Found	Theory. $C_3H_6I_2$
I	85·46 per cent.	85·81 per cent.

Trimethylene iodide boils at 215—220° (720 mm.) almost without decomposition. It does not solidify at —10°. The sp. gr of a specimen dried over phosphoric anhydride was determined by my father with the following results:—

$$d\frac{4^\circ}{4^\circ} = 2{\cdot}59617,$$

$$d\frac{15^\circ}{15^\circ} = 2{\cdot}57612,$$

$$d\frac{25^\circ}{25^\circ} = 2{\cdot}56144.$$

On trying the action of this iodide on ethylic malonate, it was soon found it presented no advantage as compared with the bromide. Not only was the yield of ethylic tetramethylenedicarboxylate no better, the boiling point of the latter and of the iodide being nearly the same, it was much more difficult to obtain a pure product. This method was therefore abandoned.

A short notice on trimethylene iodide was published in the *Berichte*

(18, 221), and shortly afterwards (*ibid.*, 18, 519) Louis Henry stated that he also had prepared this compound in a way similar to that described above, and remarked that Freund (*Monatsh. Chem.*, 2, 640) had also obtained it by heating trimethylene glycol with hydriodic acid.

Louis Henry states that trimethylene iodide boils at 224° (763 mm.), and does not solidify at −20°. He also makes some interesting remarks on the stability of this compound as compared with ethylene iodide.

Theoretical Remarks.

In the foregoing, the substances produced by the action of trimethylene bromide on ethylic malonate have, without comment, been taken as being derivatives of tetramethylene. This is, however, not necessarily the case. There is another interpretation of this reaction, which at first sight is quite as probable, and that is, that these compounds are really nothing more than allyl-derivatives, thus: ethylic tetramethylenedicarboxylate, tetramethylenedicarboxylic acid, and tetramethylenemonocarboxylic acid might be ethylic allylmalonate, allylmalonic acid, or allylacetic acid respectively.

Such derivatives could easily be formed in the following way:—

The first product of the action of trimethylene bromide on ethylic malonate would be undoubtedly ethylic bromopropylmalonate, thus:—

$$CHNa(COOC_2H_5)_2 + CH_2Br{\cdot}CH_2{\cdot}CH_2Br = CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2 + NaBr.$$

In the second phase of the reaction, two changes can take place, that is: (*α*) the bromine-atom can combine with the hydrogen-atom of the CH-group, in which case ethylic tetramethylenedicarboxylate would be formed, or (*β*) hydrogen bromide may be eliminated in the following way:—

$$CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2 = CH_2{:}CH{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2 + HBr.$$

ethylic allylmalonate being produced.

This being the case, it will be necessary, before going further, to prove that the products of the action of trimethylene bromide on ethylic malonate are really tetramethylene-derivatives, and not allyl-derivatives.

Here the proof is fortunately much easier than was the case with ethylic trimethylenedicarboxylate and ethylic vinylmalonate described in Part I of this research (Trans., 1886, 817), all the corresponding allyl-derivatives having already been prepared and examined, and it is therefore only necessary to compare these side by side with the tetramethylene compounds, in order to show at a glance the remarkable differences existing between them.

This is shown very clearly on examining the following table of the boiling and melting points of the two series of compounds :—

(*α.*) *Boiling Points.*

	(760 mm.).		(760 mm.).
Ethylic tetramethylenedicarboxylate	224—225°	Ethylic allylmalonate	219—220°
Tetramethylene-monocarboxylic acid	194—195	Allylacetic acid......	183°
Ethylic tetramethylenemonocarboxylate	154—155	Ethylic allylacetate ..	142—144°

(*β.*) *Melting Points.*

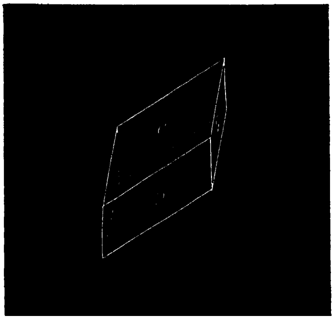
Tetramethylene - dicarboxylic acid	154—156°	Allylmalonic acid ..	103°

These two melting points show a variation of 50°. In order, however, to establish the great difference between tetramethylenedicarboxylic acid and allylmalonic acid, I submitted some beautiful crystals of the latter to Professor Haushofer, who kindly measured them for me with the following results :—

Monallylmalonic Acid.

Crystalline system : triclinic.

Small brilliant crystals resembling rhombohedrons, of which the faces *c*, *p*, and *q* were observed; cleavage perfect conformably to the surface *q*.

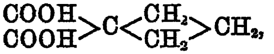


Measured.

$p : q =$ 43° 58′ (front)
$q : c =$ 97 2
$p : c =$ 114° 39

On comparing the crystalline form of this acid with that of tetramethylenedicarboxylic acid (given on page 5), it is at once evident that the two acids cannot possibly be identical.

Professor Franchimont (*Rec. Trav. Chim.*, 1885, 398 and 399) has lately published a series of researches on the action of pure nitric acid on organic compounds, and, among others, on the derivatives of malonic acid. He found that malonic acid and its monosubstituted derivatives, such as ethyl-allylmalonic acid, &c., were completely decomposed when treated with pure nitric acid, with elimination of 2 mols. CO_2. The disubstituted malonic acids, such as diethylmalonic acid, &c., were on the contrary not acted on at all when left in contact with this acid. In connection with these experiments, Professor Franchimont was kind enough to examine the behaviour of tetramethylenedicarboxylic acid when treated with pure nitric acid, and found that this compound, even after standing for days with nitric acid, showed no signs of decomposition, and after 10 days' exposure, he was able, on extracting with ether, to regain nearly the whole of the tetramethylenedicarboxylic acid unchanged.

These experiments can only be explained on the assumption that the tetramethylenedicarboxylic acid is a disubstituted malonic acid of the formula  $\genfrac{}{}{0pt}{}{COOH}{COOH}>C<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>CH_2$, and they therefore go far to prove that this compound is really a tetramethylene-derivative.

An equally conclusive proof of the constitution of this acid can be deduced from the study of the magnetic rotations of ethylic tetramethylenedicarboxylate and tetramethylenemonocarboxylic acid. The magnetic rotation of ethylic tetramethylenedicarboxylate is 9·940, that of tetramethylenecarboxylic acid is 5·048. The difference between the magnetic rotation of these two substances and those of the isomeric allyl* derivatives is very striking. Thus:

The magnetic rotation of the allylmalonate = 11·281.
" " allylacetic acid = 6·426.

Here the differences between the magnetic rotation of ethylic allymalonate and ethylic tetramethylenedicarboxylate, and between those of allylacetic acid and tetramethylenecarboxylic acid, are 1·378 resp. 1·341, a further proof that these compounds cannot possibly be identical.

The magnetic rotations of these tetramethylene-derivatives agree much more closely with those of the corresponding saturated compounds in the fatty series, allowing of course in all cases for the difference of $H_2 = 0·508$. Thus:

---

* W. H. Perkin, Trans., 1884, 44, 508, 576, and 1886, 49, 211.

Ethylic propymalonate —2H = 9·859.
Valeric acid —2H = 5·000.

It would appear from the experiments which have up to the present time been carried out by my father, that the value of CH_2 in a ring is slightly different from the value of CH_2 in an open chain.

The study of the magnetic rotation of these tetramethylene-derivatives also shows that both tetramethylenedicarboxylic and tetramethylenemonocarboxylic acids are derivatives of the same group of elements, that is $CH_2<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>CH_2$.

Thus if the value of ethylic malonate $-2H = 6·902$ be abstracted from the value of ethylic tetramethylenedicarboxylate (9·940), we get 3·038 as the value of the group $\genfrac{}{}{0pt}{}{—CH_2}{—CH_2}>CH_2$.

If a similar operation be performed with tetramethylenemonocarboxylic acid, we get the following:—

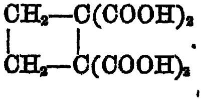
Tetramethylenemonocarboxylic acid (5·048)—Acetic acid —2H (2·017) = 3·031 = value of $\genfrac{}{}{0pt}{}{—CH_2}{—CH_2}>CH_2$, a number closely agreeing with the preceding one.

Dr. Gladstone's measurements of the refraction and dispersion equivalents of ethylic tetramethylenedicarboxylate and tetramethylenemonocarboxylic acid also show closely that these must be saturated compounds. Dr. Gladstone has given me the following explanation of the results of his determinations (pp. 4, 11, 12).

"The refraction and dispersion equivalents of *ethylic tetramethylenedicarboxylate* indicate that it is a saturated body.

"*Tetramethylenecarboxylic acid.*—These figures closely agree with those of a saturated compound, an allyl compound gives much higher figures. (The refraction equivalent of allylacetic acid is 43·25, and the dispersion equivalent 2·41.)"

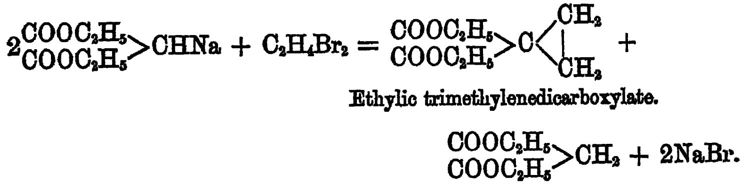
There can therefore scarcely be a doubt, but that the compounds produced by the action of trimethylene bromide on ethylic malonate are really derivatives of tetramethylene.

II. *Tetramethylenetetracarboxylic acid* (1, 1, 2, 2,) 

$$\begin{array}{l} CH_2—C(COOH)_2 \\ |\qquad\quad | \\ CH_2—C(COOH)_2 \end{array}.$$

If the sodium compound of ethylic malonate be treated with ethylene bromide, the principal product of the reaction is ethylic trimethylenedicarboxylate (1, 1), as was shown in Part I of this research, Trans., 1885, p. 807.*

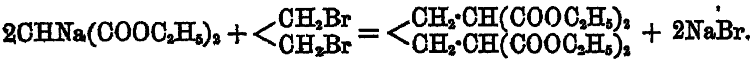
This compound is formed according to the following equation, one molecule of ethylene bromide reacting with one molecule of ethylic malonate:—



Ethylic trimethylenedicarboxylate.

This ethereal salt is, however, not the only product of the reaction, as there is always a small quantity of an oil of high boiling point formed at the same time: this remains behind in the retort during the purification of the crude product, after the ethylic trimethylenedicarboxylate has distilled over. (See Part I, Trans., 1885, p 808.)

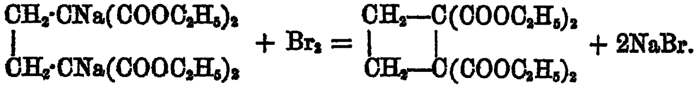
This oil, after being carefully fractioned under diminished pressure, proved to be the product of the action of 1 mol. of ethylene bromide on 2 mols. of the sodium compound of ethylic malonate, thus:—



$$2CHNa(COOC_2H_5)_2 + <\begin{matrix}CH_2Br\\ CH_2Br\end{matrix} = <\begin{matrix}CH_2\cdot CH(COOC_2H_5)_2\\ CH_2\cdot CH(COOC_2H_5)_2\end{matrix} + 2NaBr.$$

This substance, for which I propose the name ethylic butane-$\omega_2\omega_2$-tetracarboxylate,† can with advantage be used for the synthesis of tetramethylene compounds.

When mixed with sodic ethylate, two of its hydrogen-atoms are directly displaced by sodium, forming a disodium compound which when treated with bromine is converted quantitatively into the ethereal salt of tetramethylenetetracarboxylic acid (1, 1, 2, 2), thus:—



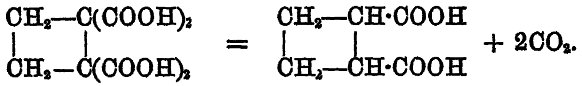
Disodium compound. Ethylic tetramethylenetetracarboxylate (1, 1, 2, 2).

On hydrolysis, the free acid is easily obtained, and this in its turn when heated at 180°, splits up into tetramethylenedicarboxylic acid (1, 2) and 2 mols. CO_2, thus:—

---

* See also *Berichte*, 17, 54, 323; 18, 1734; 19, 1049. Fittig and Roeder, *Annalen*, 227, 13.

† With regard to the nomenclature, see Baeyer (*Ber.*, 17, 961).



$$\begin{array}{l}CH_2\text{—}C(COOH)_2\\ |\qquad\;\; |\\ CH_2\text{—}C(COOH)_2\end{array} = \begin{array}{l}CH_2\text{—}CH\cdot COOH\\ |\qquad\;\; |\\ CH_2\text{—}CH\cdot COOH\end{array} + 2CO_2.$$

Tetramethylene-tetracarboxylic acid (1, 1, 2, 2). Tetramethylene-dicarboxylic acid (1, 2).

As this reaction appeared to be of special interest, it was worked out very carefully, the following being the details of the processes used.

Ethylic Butane-$\omega_2\omega_2$-Tetracarboxylate,

$(COOC_2H_5)_2CH\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2$.

In order to obtain this substance, which is the starting point in the following syntheses, the crude product of the action of ethylene bromide on ethylic malonate (prepared as described in Trans., 1885, p. 807) is submitted to distillation in steam until oily drops cease to come over. By this means, all the ethylic trimethylenedicarboxylate, together with unchanged ethylene bromide and ethylic malonate, are carried over by the steam, a small quantity of a thick yellowish oil being left in the retort, which can be easily separated from the watery liquid by extracting once or twice with ether. After drying over calcic chloride and distilling off the ether, the crude ethylic butanetetracarboxylate is obtained as a thick yellowish oil, which is next purified by fractioning under diminished pressure (225 mm.); it then nearly all goes over between 250 and 290° the first time, and on repeatedly fractioning a colourless oil is obtained boiling constantly at 275—280°. This gives the following numbers on analysis:—

0·1620 gram substance gave 0·1118 gram H_2O and 0·3280 gram CO_2.

	Found.	Theory. $C_{16}H_{26}O_8$.
C......	55·22 per cent.	55·49 per cent.
H......	7·66 „	7·51 „
O......	37·12 „	36·99 „

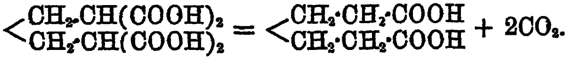
Ethylic butane-$\omega_2\omega_2$-tetracarboxylate is a thick, colourless oil of feeble odour; it does not solidify at 0°. The yield obtained by the above method is very small; 10 grams from 300 grams of ethylic malonate has rarely been exceeded.

The boiling points of this compound incidentally observed are

At 100 mm. = 248—252°
„ 225 „ = 275—280.

In order to prove that this ethereal salt really has the constitution assigned to it at the beginning of this chapter, it was next converted into butanetetracarboxylic acid by hydrolysis.

This acid is decomposed when heated to 200° into adipic acid, and 2 mols. CO_2, thus :—



$$<\begin{array}{l}CH_2\cdot CH(COOH)_2\\ CH_2\cdot CH(COOH)_2\end{array} = <\begin{array}{l}CH_2\cdot CH_2\cdot COOH\\ CH_2\cdot CH_2\cdot COOH\end{array} + 2CO_2.$$

Butane-$\omega_2\omega_2$-tetra-carboxylic acid. Adipic acid.

Thus affording a direct proof of the constitution of butanetetracarboxylic acid.

The hydrolysis of the ethereal salt of this acid is best carried out in the following way :—

The pure ethereal salt is mixed with a slight excess of alcoholic potash and heated for about four hours to boiling. Water is then added, the whole evaporated, nearly to dryness, on a water-bath, and the residue dissolved in water. The alkaline solution is next carefully neutralised with acetic acid, and the lead salt of the acid precipitated by adding excess of acetate of lead. After collecting the lead salt and washing it well with water, to remove the soluble salts, it is suspended in water and decomposed with sulphuretted hydrogen. In order to obtain the free acid, the lead sulphide is filtered off and the solution evaporated over sulphuric acid in a vacuum. In this way, the butanetetracarboxylic acid is obtained as a thick colourless oil which appears to crystallise on long standing.

The analysis of the silver salt, prepared by precipitating a neutral solution of the ammonium salt with nitrate of silver, well washing and drying over sulphuric acid in a vacuum, gave the following numbers, agreeing approximately with the formula

$$(COOH)_2CH\cdot CH_2\cdot CH_2\cdot CH(COOH)_2.$$

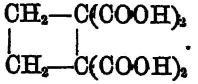
0·1083 gram substance gave 0·0696 gram silver.

	Found.	Theory.
Ag	64·27 per cent.	65·22 per cent.

If butanetetracarboxylic acid is heated in a small Würtz flask at 200°, until the evolution of carbonic anhydride ceases, and the brownish residue is then distilled, a thick colourless oil is obtained, which on long standing almost entirely solidifies to crystals of adipic acid. In order to purify these crystals, they were roughly freed from the mother-liquor by spreading out on a porous plate, and then dissolved in a small quantity of water. This solution was allowed to evaporate over sulphuric acid in a vacuum, when beautiful colourless crystals melting at 146—148° were obtained. (Adipic acid melts at 149°.)

Unfortunately the quantity was too small for analysis, but there can be no doubt, from the appearance, melting point, and general properties that the substance was really adipic acid.

Tetramethylenetetracarboxylic acid (1, 1, 2, 2),



$$\begin{array}{l} CH_2—C(COOH)_2 \\ \;|\qquad\;\;| \\ CH_2—C(COOH)_2 \end{array}.$$

If the ethereal solution of 1 mol. ethylic butanetetracarboxylate is mixed with an ethereal solution of sodic ethylate (2 mols.), and the whole allowed to remain for a short time, the disodium compound of the above ethereal salt is precipitated in colourless flocks; this, after collecting and washing with a mixture of alcohol and ether, is approximately pure, giving the following number on analysis:—

0·2221 gram substance gave 0·0778 gram Na_2SO_4.

	Found.	Theory. $(COOC_2H_5)_2CNa\cdot CH_2\cdot CH_2\cdot CNa(COOC_2H_5)_2$.
Na......	11·35 per cent.	11·79 per cent.

This disodium compound is fairly stable and dissolves in water forming a clear solution, which however on standing or on the addition of an acid is decomposed, an oil, probably unchanged ethylic butanetetracarboxylate, separating out.

This disodium compound, when treated with bromine, is converted into ethylic tetramethylenetetracarboxylate. This synthesis of the tetramethylene-ring is carried out in the following way:—21 grams of pure ethylic butanetetracarboxylate are dissolved in about 100 grams of pure dry ether, and then mixed with an ethereal solution of sodic ethylate containing 3 grams of sodium;* the whole being allowed to stand about five minutes to ensure the complete precipitation of the sodium compound. 10 grams of pure bromine are now slowly added through a dropping funnel, the whole being well agitated and cooled during the operation. Each drop of bromine becomes instantly decolorised as it comes in contact with the sodium compound, but the last drop of bromine should cause a faint but permanent yellowish coloration of the solution; as soon as this takes place, the reaction is complete. After standing for about an hour, water is added, the ethereal solution separated from the aqueous layer, well washed with water and carbonate of soda solution, and dried over calcic chloride. On distilling off the ether, the crude ethylic tetramethylenetetracarboxylate is obtained as a thick colourless oil, which was not further purified, but used as it was for preparing the free tetramethylenetetracarboxylic acid. This was done in the following way:—

---

* Prepared by dissolving the calculated quantity of sodium in as little hot alcohol as possible, and then while still hot, pouring in about five times the volume of pure dry ether.

The crude ethereal salt was mixed with a solution of 16 grams of pure potash dissolved in a little alcohol, and boiled for about eight hours. Water was then added and the solution evaporated nearly to dryness on a water-bath, in order to drive off the alcohol as completely as possible. The residue was then dissolved in water, neutralised with acetic acid, and the lead salt of the acid precipitated by adding acetate of lead. The thick white precipitate thus obtained was then carefully washed with water, until quite free from soluble inorganic matter, suspended in water, and decomposed with sulphuretted hydrogen. After filtering off the precipitated sulphide of lead, the filtrate was allowed to evaporate over sulphuric acid in a vacuum, when a colourless oil was left, which, after a short time, solidified to a mass of crystals. These were first purified by spreading out on a porous plate, then washed once or twice with benzene, and dried over sulphuric acid in a vacuum.

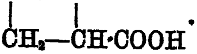
The analysis gave the following results:—

0 0675 gram substance gave 0·0231 gram H_2O and 0·1015 gram CO_2.

	Found.	Theory. $C_4H_4(COOH)_4$.
C......	41·01 per cent.	41·38 per cent.
H......	3·78 „	3·45 „
O......	55·21 „	55·17 „

Tetramethylenetetracarboxylic acid (1, 1, 2, 2) is a colourless crystalline mass, which melts at 145—150°, being at the same time decomposed into tetramethylenedicarboxylic acid (1, 2) and carbonic anhydride. It is very easily soluble in water, alcohol, and ether, but more sparingly in benzene and light petroleum. The aqueous solution has a strongly acid reaction.

Tetramethylenedicarboxylic acid (1, 2),



$$\begin{array}{l}CH_2\text{—}CH\cdot COOH \\ \vert \qquad\quad \vert \\ CH_2\text{—}CH\cdot COOH\end{array}.$$

Tetramethylenetetracarboxylic acid (1, 1, 2, 2), when heated a few degrees above its melting point, is rapidly decomposed into carbonic anhydride and tetramethylenedicarboxylic acid (1, 2), as described above. During this process, however, a slight decomposition appears to take place, as the resulting mass is generally somewhat brownish, and it was thought possible that if a solution of the acid, instead of the dry substance, was heated up to the required temperature, this might be avoided and a cleaner product obtained. A fairly concentrated solution of the tetracarboxylic acid in water was therefore heated in a sealed tube for two days at 180—200°. On opening the tube, a considerable pressure was noticeable due to carbonic anhydride. In order to isolate the new acid, the aqueous solution, which was nearly colourless, was evaporated on a water-bath to a syrupy consistence; this, however, showed no signs of crystallising, even after standing for days over sulphuric acid in a vacuum.

The following method of purification was then resorted to with good results:—The crude acid was dissolved in about three times its weight of absolute alcohol, and saturated with hydrogen chloride. After standing for a few hours, water was added, and the oily drops which separated were extracted with ether. The ethereal solution, after well washing with water and dilute sodic carbonate, was distilled on a water-bath, when the ethereal salt of tetramethylenedicarboxylic acid was left as a yellowish oil. This was first distilled under diminished pressure (100 mm.), and then fractioned under the ordinary pressure. In this way, a colourless oil was obtained boiling at 238—242° (720 mm.), which gave the following numbers on analysis:—

0·1711 gram substance gave 0·1290 gram H_2O and 0·3754 gram CO_2.

	Found.	Theory. $C_4H_6(COOC_2H_5)_2$.
C......	59·83 per cent.	60·00 per cent.
H......	8·38 ,,	8·00 ,,
O......	31·79 ,,	32·00 ,,

Ethylic tetramethylenedicarboxylate (1, 2), is a colourless oil of feeble odour, boiling at 238—242°. It is isomeric with ethylic tetramethylenedicarboxylate (1, 1), which however boils at a much lower temperature, viz., 223°.

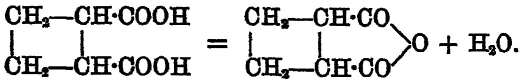
In order to obtain the free acid, the ethereal salt was boiled with an excess of alcoholic potash for three hours, the product diluted with water, evaporated on a water-bath to drive off the alcohol, and then acidified with dilute sulphuric acid. The resulting solution was several times extracted with pure ether, the ethereal solution dried over calcic chloride, and the ether distilled off, when an almost colourless crystalline mass was left, consisting of nearly pure tetramethylenedicarboxylic acid (1, 2). This was further purified by dissolving it in a small quantity of water, filtering, and allowing the solution to evaporate over sulphuric acid in a vacuum. In this way, colourless feathery crystals were obtained, which, after drying at 120°, gave the following numbers on analysis:—

I. 0·1108 gram substance gave 0·0570 gram H_2O and 0·2016 gram CO_2.

II. 0·1477 gram substance gave 0·0797 gram H_2O and 0·2689 gram CO_2.

	Found.			Theory. $C_4H_6(COOH)_2$.	
	I.	II.			
C	49·62	49·65	per cent.	50·00	per cent.
H	5·70	5·99	,,	5·56	,,
O	44·68	44·36	,,	44·44	,,

Tetramethylenedicarboxylic acid (1, 2) melts at 130°. It is easily soluble in alcohol, ether, and water, but only sparingly in light petroleum and benzene. It is isomeric with tetramethylenedicarboxylic acid (1, 1) (p. 4), which melts at 154—156°. The difference between these two acids is most apparent from their behaviour on heating. Tetramethylenedicarboxylic acid (1, 1) decomposes below 170° into carbonic anhydride and tetramethylenemonocarboxylic acid, whereas tetramethylenedicarboxylic acid (1, 2) is not changed at this temperature, but at 300°, it is converted into its anhydride, thus:—



Tetramethylenedicarboxylic acid (1, 2) is also isomeric with ethylfumaric acid, diacrylic acid, tetrylenedicarboxylic acid, allymalonic acid, &c. It is easily oxidised by permanganate of potash in alkaline solution, oxalic acid being formed.

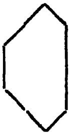
The salts of tetramethylenedicarboxylic acid (1, 2) are well characterised.

The *silver* salt is easily obtained on adding nitrate of silver to a neutral solution of the ammonium salt, as a white amorphous precipitate, sparingly soluble in water. The analysis gave the following numbers:—

0·0965 gram of substance gave 0·0575 gram of Ag.

	Found.	Theory. $C_6H_6O_4Ag_2$.
Ag......	59·58 per cent.	60·33 per cent.

The most characteristic salt, however, is the *barium* salt. If baric chloride is added to a fairly concentrated solution of the ammonium salt, no precipitate is formed and the liquid remains clear. If heat be now applied, as soon as the boiling point is reached, the barium salt is precipitated as a colourless crystalline powder, which, when examined under the microscope, is found to consist of six-sided plates, having the form



This barium salt in the crystalline form is sparingly soluble in both hot and cold water.

A solution of the ammonium salt behaves as follows when treated with the following salts:—

Plumbic acetate, white precipitate, sparingly soluble in water.

Cupric sulphate, added to a cold solution of the ammonium salt, gives no precipitate. On boiling, however, the copper salt is thrown down as a light-green amorphous mass.

Calcic chloride } No precipitates.
Zincic sulphate }

Anhydride of Tetramethylenedicarboxylic Acid (1, 2).

Tetramethylenedicarboxylic acid, when heated at 300° for half an hour, is completely converted into its anhydride. On distilling the product, a colourless oil is obtained, which solidifies on cooling to a hard crystalline mass of the nearly pure anhydride. After powdering, washing with a little ether, and drying over sulphuric acid in a vacuum, the following results were obtained on analysis:—

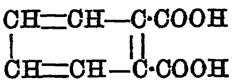
0·1206 gram substance gave 0·0552 gram H_2O and 0·2531 gram CO_2.

	Found.	Theory. $C_4H_6 : C_2O_3$.
C......	57·23 per cent.	57·14 per cent.
H......	5·09 „	4·76 „
O......	37·68 „	38·10 „

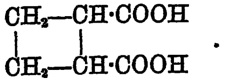
This anhydride, purified as described above, melts at 76—78°. It is easily soluble in alcohol, but more sparingly in ether and benzene. In contact with water, it is only very slowly decomposed at ordinary temperatures, but on boiling it is rapidly converted into tetramethylenedicarboxylic acid.

If this anhydride is heated with resorcinol for some time at 250°, a reddish-coloured melt is obtained, which, when dissolved in water and treated with ammonia, gives the fluoresceïn reaction in the most beautiful manner.

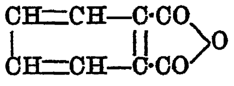
Tetramethylenedicarboxylic acid (1, 2) and its anhydride are more especially interesting, as they are those derivatives of tetramethylene which correspond with phthalic acid and its anhydride in the aromatic series.



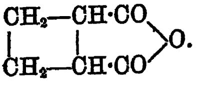
Phthalic acid.



Tetramethylenedicarboxylic acid (1, 2).



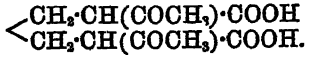
Phthalic anhydride.



Anhydride.

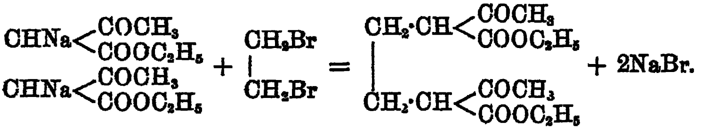
On comparing these two series of compounds, it will be seen that there is a marked resemblance in some of their properties.

III. *Diacetyltetramethylenedicarboxylic Acid* (1, 2, 1, 2),



$$<\begin{matrix}CH_2\cdot CH(COCH_3)\cdot COOH\\ CH_2\cdot CH(COCH_3)\cdot COOH.\end{matrix}$$

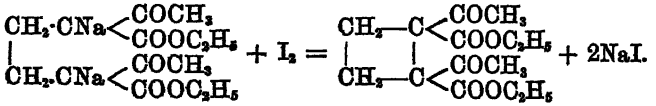
If ethylic sodacetacetate is treated with ethylene bromide, ethylic acetyltrimethylenecarboxylate is formed (Trans., 1885, 829). Besides this ethereal salt, however, another substance can be isolated, which corresponds very closely with ethylic butane-$\omega_2\omega_2$-tetracarboxylate, 2 mols. of ethylic sodacetoacetate reacting with 1 mol. of ethylene bromide, thus :—



$$\begin{matrix}CHNa{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\\ CHNa{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\end{matrix} + \begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} = \begin{matrix}CH_2\cdot CH{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\\ |\\ CH_2\cdot CH{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\end{matrix} + 2NaBr.$$

The examination of this compound, which has received the name ethylic diacetyladipate, has been carried out jointly with M. Obrembsky, and I hope to have the honour of laying a full account of it before the Society in a short time.

If this substance is treated with sodic ethylate, a disodium compound is formed which, on the addition of iodine, is converted into ethylic diacetyltetramethylenedicarboxylate (1, 2, 1, 2,) thus :—



$$\begin{matrix}CH_2\cdot CNa{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\\ |\\ CH_2\cdot CNa{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\end{matrix} + I_2 = \begin{matrix}CH_2{-}C{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\\ |\quad\ \ |\\ CH_2{-}C{<}\begin{matrix}COCH_3\\ COOC_2H_5\end{matrix}\end{matrix} + 2NaI.$$

By hydrolysis, this ethereal salt can easily be converted into diacetyltetramethylenedicarboxylic acid, which is a beautifully crystalline substance melting at 210°. This synthesis is best carried out in the following way:—

Pure ethylic diacetyladipate is dissolved in pure ether, and then the calculated amount of an ethereal solution of sodic ethylate* poured in. As soon as the sodium compound is completely formed, the calculated quantity of iodine, dissolved in ether, is added, the whole being well cooled during the operation. At first the colour of the iodine disappears instantly, but after about two-thirds has been added the reaction becomes much more sluggish, and it rarely happens that the whole of the iodine solution is decolorised.

In order to isolate the product of the reaction, water is added and sufficient sulphurous acid to decolorise the liquid completely. The ethereal solution is then separated from the aqueous layer, well washed with water, dried over calcic chloride, and the ether distilled off. The residual oil was not further purified but directly converted into the free acid by hydrolysis. For this purpose, the crude oil was boiled with an excess of a moderately concentrated solution of alcoholic potash, for about three hours, the product evaporated to dryness on a water-bath, and the residue dissolved in water. The brownish solution when acidified with dilute sulphuric acid deposited an uninviting tarry mass, which it was found almost impossible to purify. After many trials, the following method was found to give the best results. The brown alkaline solution obtained by hydrolysis with potash, as described above, was carefully neutralised with dilute sulphuric acid, boiled with freshly ignited animal charcoal, and filtered. The filtrate, which was still somewhat dark coloured, was then acidified with dilute sulphuric acid and well agitated in a stoppered bottle at a temperature of about 40—50°. In this way almost all the resinous matter balled together, leaving a nearly colourless solution of diacetyltetramethylenedicarboxylic acid. In carrying out this method, it is of course necessary to have sufficient water present to dissolve the acid, but too much should be avoided, as a less pure product is then obtained. In order to extract the acid from this solution, the liquid after filtering was four or five times shaken up with ether, and the ethereal solution well dried over chloride of calcium. On distilling off the ether, the acid was precipitated in the form of hard yellowish crusts, and was easily obtained pure by crystallisation from water.

Diacetyltetramethylenedicarboxylic acid (1, 2, 1, 2) crystallises from water in colourless glittering plates which contain 2 mols. H_2O:—

I. 0·1509 gram substance gave 0·0853 gram H_2O and 0·2520 gram CO_2.

---

* See footnote, p. 21.

II. 0·3015 gram substance dried at 80—90° lost 0·0406 gram H_2O.
III. 0·3664 gram substance dried at 100—110° lost 0·0498 gram H_2O.

	Found.			Theory.
	I.	II.	III.	$C_4H_4(C_2H_3O)_2(COOH)_2+2H_2O$.
C......	45·54	—	—	45·45 per cent.
H	6·28	—	—	6·06 „
O......	—	—	—	34·86 „
H_2O ...	—	13·46	13·59 per cent.	13·63 „

These crystals part with their water of crystallisation slowly when placed over sulphuric acid in a vacuum, but much more quickly at 80°; they then lose their lustre altogether and become opaque. The analysis of the dry substance crystallised once from ether gave the following results:—

0·1740 gram substance gave 0·3335 gram CO_2 and 0·0874 gram H_2O.

	Found.	Theory. $C_{10}H_{12}O_6$.
C	52·27 per cent.	52·63 per cent.
H......	5·58 „	5·26 „
O	42·15 „	42·11 „

Diacetyltetramethylenedicarboxylic acid melts at 210°, being at the same time decomposed into carbonic anhydride and oils of high boiling point and disagreeable odour; as the quantity of material at my disposal was but small, these could not be further examined. The acid is easily soluble in alcohol, ethyl acetate, and hot water, but little soluble in benzene, light petroleum, chloroform, and cold water.

In conclusion, I append the following list of the substances described in the paper:—

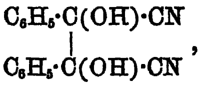
Name.	Boiling point.	Boiling point (720 mm.) uncorr.	Boiling point of ethereal salt (720 mm.) uncorr.
Tetramethylenemonocarboxylic acid ...	—	191	151—151·5°
Tetramethylenedicarboxylic acid (1, 1)..	154—156°	—	220—221°
„ „ „ (1, 2)..	130°	—	238—242
Anhydride of tetramethylenedicarboxylic acid (1, 2)	76—78°	—	—
Diacetyltetramethylenedicarboxylic acid (1, 1, 2, 2)......................	210°	—	—
Tetramethylene tetracarboxylic acid (1, 1, 2, 2)	145—150°	—	—
Butane-$\omega_2\omega_2$-tetracarboxylic acid	145—150	—	—

II.—*Preparation and Hydrolysis of Hydrocyanides of the Diketones.*

By **Francis R. Japp**, F.R.S., and **N. H. J. Miller**, Ph.D.

The first hydrocyanide of a diketone—benzil dihydrocyanide—was discovered by Zinin, who prepared it by dissolving benzil in boiling alcohol and adding about an equal weight of nearly anhydrous hydrocyanic acid. A compound of 2 mols. of hydrocyanic acid with 1 mol. of benzil, $C_{14}H_{10}O_2(HCN)_2$, was obtained. According to Zinin, this compound is not altered by boiling with water or with hydrochloric acid.

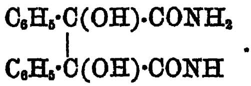
As the compound may be regarded as a nitrile of diphenyltartaric acid, thus—



$$\begin{array}{l}C_6H_5\cdot C(OH)\cdot CN\\ \quad\quad\;\,|\\ C_6H_5\cdot C(OH)\cdot CN\end{array},$$

we determined to study its behaviour towards hydrolytic agents, in order, if possible, to obtain this acid. With a similar view, we prepared the hitherto unknown hydrocyanide of phenanthraquinone, in order to arrive at the corresponding diphenylenetartaric acid.

We had been engaged on this work for some time, when a preliminary note on the same subject was published by B. S. Burton (*Ber.*, 16, 2232). Guided by the same idea, this author had studied the action of hydrolytic agents upon Zinin's compound. By subjecting it to the action of a solution of hydrobromic acid in glacial acetic acid, he succeeded in obtaining, not diphenyltartaric acid, but its amide—



$$\begin{array}{l}C_6H_5\cdot C(OH)\cdot CONH_2\\ \quad\quad\;\,|\\ C_6H_5\cdot C(OH)\cdot CONH\end{array}.$$

As this work differed from our own, both in the experimental conditions adhered to and in the results obtained, we at once published a preliminary note (*Ber.*, 16, 2416) giving a brief account of the research upon which we were engaged. The object of the present paper is to supplement, and in some respects to correct, the statements made in that preliminary publication.

Benzil Dihydrocyanide.

In the reaction about to be described, we did not isolate the benzil dihydrocyanide; indeed, we afterwards found that, with the pure compound, no action occurs. The following method was employed:—

Benzil was dissolved in a quantity of alcohol sufficient to retain in solution the dihydrocyanide which is formed, and a considerable excess of anhydrous hydrocyanic acid was added. The liquid was then saturated with gaseous hydrochloric acid, cooling with ice-water during the operation, after which it was allowed to stand for some weeks. On pouring the solution into water, a yellow viscid substance separated, the quantity of which was increased by exposing the whole for some days to the air in a shallow vessel, in order that the excess of alcohol might evaporate. The viscid substance was boiled with a solution of sodium carbonate, which extracted an acid. The residue was dissolved in boiling alcohol, and, on cooling, separated in lustrous, pale-yellow laminæ or flat needles, melting constantly at 196—197°; some also separated from the hot sodium carbonate solution on cooling. It is sparingly soluble in boiling water and benzene, readily soluble in boiling alcohol. Warm strong hydrochloric acid dissolves it on cooling, and deposits *colourless* laminæ; these. if washed with water or dilute hydrochloric acid, or on drying, become yellow again. The yellow compound, therefore, apparently possesses weak basic properties, forming unstable colourless salts.

Analysis of the yellow compound gave figures which led to the formula $C_{16}H_{12}N_2O$:—

	Substance.	CO_2.	H_2O.
I	0·1502	0·4263	0·0728
II	0·1198	0·3390	0·0558

III. 0·1032 gram, burnt with copper oxide in a vacuum, gave 9·8 c.c. of moist nitrogen at 21°, and under 758·5 mm. pressure.

	Calculated for $C_{16}H_{12}N_2O$.		Found.		
			I.	II.	III.
C_{16}	192	77·42	77·41	77·17	—
H_{12}	12	4·84	5·39	5·17	—
N_2	28	11·29	—	—	10·78
O	16	6·45	—	—	—
	248	100·00			

Different preparations were analysed.

The compound contains in its molecule an atom of oxygen less than benzil dihydrocyanide :—

$$\underset{\text{Benzil dihydrocyanide.}}{C_{16}H_{12}N_2O_2} = \underset{\text{New compound.}}{C_{16}H_{12}N_2O} + O.$$

It may be heated with fuming hydrochloric acid at 170° without undergoing any change beyond being converted into the unstable salt above referred to.

Aqueous potash is without action upon it.

The yield of the substance was very small, and we were therefore unable to undertake the study of its decompositions.

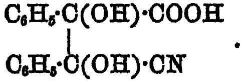
In the above reaction, the benzil dihydrocyanide is for the most part converted into acids. If the alcoholic solution of benzil, hydrocyanic acid, and hydrochloric acid is allowed to stand too long, the aqueous solution which is obtained after the separation of the viscid yellow substance contains a mixture of acids, which we found it impossible to separate. On one occasion, however, we succeeded in isolating a nitrogenous acid which dissolved in boiling water and, on cooling, was deposited in colourless prisms melting at 196°. The analytical figures pointed to the formula $C_{16}H_{13}NO_4$:—

	Substance.	CO_2.	H_2O.
I	0·1160	0·2876	0·0506

II. 0·1144, burnt with copper oxide in a vacuum, gave 5·0 c.c. of moist nitrogen at 20·7° and under 768 mm. pressure.

	Calculated for $C_{16}H_{13}NO_4$.		Found.	
			I.	II.
C_{16}......	192	67·84	67·62	—
H_{13}.....	13	4·59	4·85	—
N	14	4·95	—	5·03
O_4......	64	22·62	—	—
	283	100·00		

This is the formula of an acid which would be derived from benzil dihydrocyanide by the conversion of one cyanogen-group into carboxyl :—



$$\begin{array}{l} C_6H_5\cdot C(OH)\cdot COOH \\ \quad\quad\;\; | \\ C_6H_5\cdot C(OH)\cdot CN \end{array}.$$

The quantity of substance at our disposal was unfortunately insufficient for further examination.

Benzil dihydrocyanide may be readily prepared by passing a large excess of gaseous hydrocyanic acid into alcohol in which benzil is suspended, cooling during the process. On standing for some days, the benzil gradually dissolves, whilst white crystals of the dihydrocyanide are deposited.* After washing with alcohol in the cold, the crystals are practically pure.

---

* We also noticed the formation of ethylic benzoate, a decomposition already

Benzil dihydrocyanide dissolves in strong alcoholic hydrochloric acid, but appears to undergo little or no change. The compounds above described are not formed under these conditions.

Phenanthraquinone Dihydrocyanide.

This compound had not hitherto been prepared. The method employed in the preparation of the benzil-compound was first tried, but failed to yield the new compound in a condition suitable for analysis, as alcohol, even when considerably diluted with water, retained it in solution. The following plan was adopted with success :—

Very finely powdered phenanthraquinone was treated in the cold with a large excess of aqueous 30 per cent. hydrocyanic acid (a more dilute acid is almost without action), shaking the flask from time to time. The quinone assumed a vermilion colour; at the same time, part of it dissolved. The liquid soon began to deposit tufts of very slender white needles. The moment this separation commenced the liquid was quickly filtered, in order to remove unaltered phenanthraquinone. The filtrate deposited a considerable quantity of the abovementioned needles.

When exposed in a moist state to the air, the new compound decomposed very readily. Even in drying over sulphuric acid, it turned reddish-brown on the surface, owing to a regeneration of phenanthraquinone. It was therefore, after drying, washed with chloroform, to remove the phenanthraquinone, and again dried over sulphuric acid. After this treatment, the compound, which was now almost colourless, was analysed. It gave figures agreeing with the expected formula $C_{14}H_8O_2(HCN)_2$:—

	Substance.	CO_2.	H_2O.
I	0·1586	0·4243	0·0622
II	0·1085	0·2908	0·0430

III. 0·1036 gram, burnt with copper oxide in a vacuum, gave 9·65 c.c. of moist nitrogen at 19° and under 751·5 mm. pressure.

	Calculated for $C_{16}H_{10}N_2O_2$.		Found.		
			I.	II.	III.
C_{16}	192	73·28	72·96	73·09	—
H_{10}	10	3·82	4·35	4·40	—
N_2	28	10·69	—	—	10·58
O_2	32	12·21	—	—	—
	262	100·00			

described by Michael (*Amer. Chem. J.*, 7, No. 3). An excess of alcohol increases the amount of this decomposition, and is therefore to be avoided.

The melting point could not be determined, as the compound evolves hydrocyanic acid on heating, and is converted into phenanthraquinone. In a desiccator, it may be preserved for an indefinite time; but exposure to moist air speedily turns it reddish-brown. Boiling with water totally decomposes it; but it dissolves in hot dilute hydrochloric acid, and, provided too long boiling is avoided, may be recrystallised from this solvent with only slight decomposition.

The ready solubility of this compound, even in very dilute alcohol, as compared with the sparing solubility of benzil dihydrocyanide, is anomalous, as diphenylene-compounds are usually much less soluble than the corresponding diphenyl-compounds.

The above was the method employed in obtaining the compound for analysis. In studying its hydrolysis, we at first proceeded as in the case of the benzil-compound, acting with hydrochloric acid upon the compound in alcoholic solution in presence of an excess of hydrocyanic acid. Afterwards, nearly pure phenanthraquinone dihydrocyanide was treated with fuming aqueous hydrochloric acid. In order to prepare the dihydrocyanide for this purpose, the same process was employed as in the preparation of the substance for analysis, except that, instead of filtering, the mixture of finely powdered phenanthraquinone and 30 per cent. hydrocyanic acid was allowed to stand in a strong flask for two or three days, shaking from time to time, in order to break up the cake of dihydrocyanide and unchanged quinone which was formed. At the end of this time, there were only traces of quinone left, and these were visible only on treating a sample of the product with alcohol. The substance was then filtered through a cone, removing the liquid, so far as possible, by means of the filter-pump.

The substance thus prepared was introduced, without previous drying, into a stout flask, and a large excess of the strongest hydrochloric acid was added. In the first experiment made in this way, the flask was corked up and left overnight; but in the morning it was found that the cork had been blown out and the contents of the flask scattered about. In repeating the experiment, a delivery tube was therefore attached to the flask, when it was found that carbonic anhydride was given off. When this evolution of gas, which continued for some days, had ceased, water was added to the contents of the flask, and the undissolved substance was separated by filtration and dried. Two compounds, having respectively the formulæ $C_{15}H_9NO$ and $C_{15}H_{11}NO_2$,* could be isolated from it. Their separation was a matter of some difficulty.

---

* In the preliminary note already referred to, the formulæ $C_{16}H_{11}NO$ and $C_{16}H_{13}NO_2$ were erroneously assigned to these compounds. The difference in percentage composition between the C_{15} and C_{16} formulæ is very slight (*vide infra*),

The relative quantities of these two compounds formed appear to vary considerably in different experiments. In our first experiment, (in which a somewhat different method of hydrolysis was employed from that described above) we obtained the compound $C_{15}H_9NO$ by direct crystallisation of the product from benzene. Working as above, it is the compound $C_{15}H_{11}NO_2$ which is thus obtained. This last method is the most convenient, and the compound $C_{15}H_9NO$ can be obtained from the same crude product by modifying the treatment.

When therefore the crude product, prepared as above, was dissolved in boiling benzene, the solution, on cooling, deposited tufts of slender needles, which, after recrystallising several times from the same solvent, were obtained colourless, with a constant melting point of 183°.

The results of analysis agreed with the formula $C_{15}H_{11}NO_2$:—

	Substance.	CO_2.	H_2O.
I	0 1336	0·3726	0·0600
II	0·1314	0·3650	0·0604

III. 0·0820 gram gave 4·15 c.c. of moist nitrogen at 21° and under 759 mm. pressure.

	Calculated for $C_{15}H_{11}NO_2$ *		Found.		
			I.	II.	III.
C_{15}	180	75·95	76·06	75·76	—
H_{11}....	11	4·64	4·99	5·11	—
N.....	14	5·91	—	—	5·75
O_2	32	13·50	—	—	—
	237	100·00			

This compound is formed from phenanthraquinone dihydrocyanide according to the equation—

$$C_{16}H_{10}N_2O_2 + 2H_2O = C_{15}H_{11}NO_2 + NH_3 + CO_2.$$

---

affecting chiefly the hydrogen, which was found too high in the earlier analyses. At the time of writing the note, which appeared rather hurriedly on account of the publication of Burton's paper, we had not been able to examine any salts of these compounds, and we thus lacked the most important clue to their molecular weight. Moreover, in the method which we at that time employed in preparing the compounds, the evolution of carbonic anhydride escaped our notice; hence we the more readily accepted without question analytical results which appeared to prove that the compounds contained the same number of carbon-atoms as the dihydrocyanide from which they were derived.

* The formula $C_{16}H_{13}NO_2$, which was assigned to this compound in the preliminary note, requires C 76·49, H 5·18, and N 5·58 per cent.

We experienced some difficulty in obtaining the substance free from the compound $C_{15}H_9NO$, formed at the same time, as this has almost the same solubility in benzene, and is deposited from this solvent in very similar forms; the latter compound, however, is formed in smaller quantity, and remains in the benzene mother-liquors. The only satisfactory proof of the absence of the compound $C_{15}H_9NO$, which we have been able to find, is to dissolve a sample of the substance in a solution of sodium carbonate, and digest on the water-bath as long as a separation of amorphous reddish-brown matter continues—a process which requires three or four days for completion. On acidifying the filtered liquid with hydrochloric acid, there will be no precipitate if the compound $C_{15}H_9NO$ is absent. Both compounds dissolve in a solution of sodium carbonate and are precipitated on the addition of hydrochloric acid; but the compound $C_{15}H_{11}NO_2$ is decomposed by heating with the alkaline carbonate, ammonia being evolved and the above reddish-brown substance deposited; whereas the other compound is stable under these conditions.

The compound $C_{15}H_{11}NO_2$ is therefore an acid, inasmuch as it dissolves in solutions of alkaline carbonates, expelling carbonic acid, and is precipitated by stronger acids. Owing, however, to its instability in presence of bases, we were unable to obtain the salts in a condition fit for analysis. The sodium and barium salts became dark-coloured when heated to 100°; the latter salt, after drying at this temperature in order to expel water of crystallisation, contained Ba 23·67 per cent, instead of 22·49, as calculated for the formula $(C_{15}H_{10}NO_2)_2Ba$. The silver salt, obtained as a white precipitate by the addition of silver nitrate to a solution of the acid in ammonia, became black in a few seconds.

It seemed possible that, by the abstraction of the elements of water, this acid might be converted into the compound $C_{15}H_9NO$. We therefore boiled it for an hour with acetic anhydride; but, on allowing the mixture to cool, the acid crystallised out unchanged.

When heated in a test-tube to above 200°, it gave off a gas smelling strongly of ammonia, whilst at the same time a sublimate of very high melting point was formed. This was insoluble in glacial acetic acid, but dissolved in concentrated sulphuric acid with a deep-blue colour, and was therefore in all probability diphenanthryleneazotide.

When dissolved in acetic acid and oxidised with chromic anhydride, it yields phenanthraquinone.

On the first occasion on which we prepared this acid, we had extracted it from the product of the hydrolysis by heating the latter with a solution of sodium carbonate; and in our preliminary note we stated our impression that this acid had been formed from the above-mentioned anhydride (which we had already obtained and analysed) by the action of the alkali. This supposition is incorrect: the anhydride (*vide infra*) cannot be changed into this acid by any means which we have been able to discover, and so far from a digestion with sodium carbonate being necessary to the formation of the acid, the acid itself is, as above stated, merely decomposed by this treatment.

The compound $C_{15}H_9NO$, which is formed by hydrolysis along with the above acid, is best obtained pure by destroying the acid with which it is mixed. For this purpose, either the crude product of hydrolysis, or, better, the substance which collects in the benzene mother-liquors in purifying the acid, is dissolved in sodium carbonate and digested over the water-bath for several days. The liquid is filtered from the reddish-brown substance which separates, and again digested at 100° as long as any further separation occurs. From the clear solution, the compound $C_{15}H_9NO$ is precipitated on the addition of hydrochloric acid. By crystallising from benzene, and decolorising, if necessary, with animal charcoal, it is readily obtained pure. It is deposited from hot benzene solutions, on cooling, in tufts of colourless silky needles, melting constantly at 241°. At a higher temperature, it sublimes without decomposition.

The results of analysis agreed with the formula $C_{15}H_9NO$:—

	Substance.	CO_2.	H_2O.
I	0·1224	0·3678	0·0491
II	0·1312	0·3944	0·0520

III. 0·0938 gram gave 5·1 c.c. of moist nitrogen at 19° and under 756·5 mm. pressure:—

	Calculated for $C_{15}H_9NO$.*		Found.		
			I.	II.	III.
C_{15}	180	82·19	81·94	81·98	—
H_9	9	4·11	4·45	4·40	—
N.....	14	6·39	—	—	6·22
O	16	7·31	—	—	—
	219	100·00			

The formation of this compound from phenanthraquinone dihydrocyanide may be expressed by the equation—

$$C_{16}H_{10}N_2O_2 + H_2O = C_{15}H_9NO + CO_2 + NH_3.$$

---

* The formula $C_{16}H_{11}NO$ would require C 82·40, H 4·72, and N 6·01 per cent.

The compound $C_{15}H_9NO$, when heated with a solution of sodium carbonate, dissolves, expelling carbonic acid, and on cooling, the solution deposits lustrous, thin, six-sided plates of the formula

$$C_{15}H_{10}NO_2Na,4H_2O.$$

0·1949 gram of the air-dried salt lost at 100° 0·0432 gram of water. There was no further loss at 120°. The resulting 0·1517 gram anhydrous salt yielded, by ignition with sulphuric acid, 0·0414 gram of sodium sulphate.

	Calculated for $C_{15}H_{10}NO_2Na,4H_2O$.	Found.
H_2O in 100 parts........	21·75	22·17

	Calculated for $C_{15}H_{10}NO_2Na$.	Found.
Na in 100 parts	8·88	8·84

The barium salt was obtained by boiling the compound $C_{15}H_9NO$ with barium carbonate and water. It was deposited from the hot solution, on cooling, in forked crystals, having the formula

$$(C_{15}H_{10}NO_2)_2Ba,7H_2O.$$

On adding hydrochloric acid to the solutions of these salts, the compound $C_{15}H_9NO$ is at once precipitated.

The compound $C_{15}H_9NO$ is thus the "internal amide" (lactim or lactam) of an acid of the formula $C_{15}H_{11}NO_2$ (isomeric with that already described), incapable of existing in the free state.

Unlike the acid $C_{15}H_{11}NO_2$, the compound $C_{15}H_9NO$ does not yield phenanthraquinone on oxidation.

Owing to want of material, we have not been able to examine these derivatives of phenanthraquinone dihydrocyanide more thoroughly, phenanthraquinone—the starting-point in the preparation of these substances—having become of late years very difficult to obtain.

Normal School of Science,
South Kensington.

III.—*Note on some Double Thiosulphates.*

By J. B. Cohen, Ph.D., Assistant Lecturer, Owens College, Manchester.

Hydrated Potassium Cuprous Thiosulphate.

Rammelsberg found that when cupric sulphate or acetate is added to a solution of potassium thiosulphate, and the resulting green liquid is allowed to stand, sulphur-yellow crystals are deposited, consisting of a double thiosulphate of copper and potassium of the formula $K_2S_2O_3,Cu_2S_2O_3,2H_2O$. These crystals are needles grouped in clusters, and are readily decomposed on warming with water, copper sulphide being deposited. If, however, the addition of potassium thiosulphate be continued until the green colour disappears and gives place to a pale yellow tint (1 part of hydrated cupric sulphate requires about 2 parts of potassium thiosulphate), the resulting solution may be boiled for a long time, and only a very slight deposition of a brown precipitate occurs. On standing, this solution deposits a small quantity of brilliant orange-coloured crystals, which consist of groups of six-sided prisms, terminated by basal planes, and belong to the hexagonal system. The crystals were washed with cold water, dried in the air, and analysed with the following results:—

	Calculated for $Cu_2S_2O_3,2K_2S_2O_3,3H_2O$.	Found.				
		I.*	II.	III.	IV.	V.
H_2O	8·03	7·53	—	—	—	—
K........	23·21	—	23·27	23·34	—	—
Cu	18·74	—	19·62	—	19·51	19·67
S	28 57	—	—	27·57	—	—

The substance cannot be recrystallised from water, as it is scarcely soluble in the cold, and dissolves with slight decomposition in hot water. Hydrochloric acid decomposes it with evolution of sulphur dioxide and the formation of copper sulphide. Caustic soda precipitates cuprous oxide, and, if exposed to the air in contact with ammonia, it dissolves, forming a blue solution. It may be distinguished from Rammelsberg's salt by its crystalline form, its greater stability in hot aqueous solution, and by the fact that the slight decomposition which then occurs is not accompanied by the formation of sulphate. It may be kept unaltered in the air for several days, but slowly blackens after several weeks, even in a well-closed vessel. It immediately turns black when heated to 100—110°.

---

* Each number denotes a fresh preparation of the salt.

Anhydrous Potassium Cuprous Thiosulphate.

If 1 part hydrated copper sulphate be added to rather less than 4 parts potassium thiosulphate in hot concentrated aqueous solution, the liquid remains colourless, and, on cooling, a mass of colourless silky needles is deposited. The purification of this salt is attended with some difficulty, as, although almost insoluble in excess of potassium thiosulphate, it is very soluble in the cold in pure water. Nor can the substance be reprecipated with alcohol, as in this case almost the whole is converted into the yellow modification described above, which separates out in minute hexagonal plates. The needles were therefore freed from mother-liquor by washing them with small quantities of cold water on the filter-pump; there was considerable loss, however. The air-dried substance gave the following results on analysis, corresponding with the formula $Cu_2S_2O_3,2K_2S_2O_3$:—

	Calculated for $Cu_2S_2O_3,2K_2S_2O_3$.	Found. I.	Found. II.
Cu............	20 38	20 65	20 02

Its behaviour with reagents is similar to that of the yellow salt. It does not change colour nor lose weight at 100—110°; but begins to blacken at 120° with evolution of sulphur dioxide.

Barium Cuprous Thiosulphate.

The colourless and yellow salts both give with barium chloride the same white curdy precipitate of a barium cuprous thiosulphate, which dissolves readily in boiling water, but is scarcely soluble in cold water. The analyses of the barium salt, dried at 100—110°, gave results which apparently do not correspond with any simple formula.

	Found. I.	Found. II.	Found. III.
Ba..............	34·08	34·36	33 78
Cu..............	16·85	—	—
S	17·84	—	—

Nos. 1 and 2 are analyses of the barium compound obtained from different preparations of the yellow potassium salt; No. 3 is obtained from the anhydrous white salt.

Potassium Silver Thiosulphate.

A double thiosulphate of silver and potassium has been prepared by Herschel by adding to a solution of silver chloride in sodium thiosulphate a strong solution of potash or a potassium salt. If 2 parts of potassium thiosulphate in solution is added to 1 part of silver nitrate in solution and boiled, a black precipitate of silver sulphide is formed and sulphur dioxide evolved. On the other hand, if the solution whilst boiling be kept slightly alkaline with potassium carbonate, the amount of black precipitate is very much diminished, and the filtrate on standing deposits long colourless transparent prisms of the double salt, some of them an inch long. Analyses of the compound gave the following results, corresponding approximately with the formula $Ag_2S_2O_3,2K_2S_2O_3$.

	Calculated for $Ag_2S_2O_3,2K_2S_2O_3$.	Found.	
		I.	II.
K	22·03	—	22·19
Ag............	30·50	33·14	33·12
S	27·11	26·62	26·58

The salt does not lose weight at 100—110°, but a few brown specks make their appearance. It is decomposed by acids and alkalis, but does not change in the air nor on keeping for a length of time.

IV.—*On the Action of Silicon Tetrachloride on the Aromatic Amido-compounds.*

By Arthur Harden, B.Sc., Dalton Chemical Scholar in the Owens College.

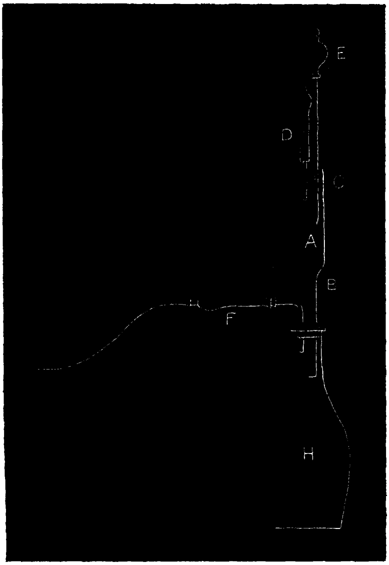
When anhydrous ammonia is passed into silicon tetrachloride, a violent reaction takes place, ammonium chloride and a nitride of silicon being formed (Deville and Wöhler, *Annalen*, **104**, 256). In order to obtain compounds in which only a portion of the hydrogen is displaced, I undertook, at the suggestion of Dr. J B. Cohen, the investigation of the action of silicon tetrachloride on the substituted ammonias, the aromatic amido-compounds being chosen on account of their greater stability.

Dichlorosilicon Diphenyldiamide, $SiCl_2(NH{\cdot}C_6H_5)_2$.

When silicon tetrachloride is added to aniline, a violent reaction takes place, accompanied by considerable development of heat, the whole solidifying to a white amorphous mass. The aniline was therefore diluted with about twice its weight of benzene which had been carefully dried over sodium, and the silicon tetrachloride, also diluted with dry benzene, was added gradually, with continual agitation, until the reaction was completed; the presence of a slight excess of the chloride being easily recognised by its characteristic acid vapour. It was then found that 1 mol. of silicon tetrachloride was required for 4 mols. of aniline.

(I.) 9 grams of aniline required 4·5 grams of $SiCl_4$. Calculated 4·1 grams.
(II.) 7·9 grams aniline required 3·6 grams $SiCl_4$. Calculated 3·8 grams.

The liquid was then filtered in a current of dry air, in order to prevent absorption of moisture and consequent decomposition. This was effected by aid of the apparatus sketched below. A wide tube A, to which one of a smaller bore has been fused at B, serves as a funnel. The opening at the wider end is closed by a cork, through which passes a calcium chloride tube D, to dry the air entering the apparatus, and a tap-funnel E, by means of which the precipitate can be washed without the admission of moist air. A plug of asbestos is placed at B, and the stem inserted in the cork of a flask H, which is connected by a conducting tube and calcium chloride tube F to an aspirator.



In practice, a current of dry air is first aspirated through the apparatus; the cork C is then removed, the liquid to be filtered poured in, the cork replaced, and the processes of filtration and washing proceeded with.

The white residue was washed with benzene and dried in a vacuum over sulphuric acid. It was readily soluble in water and alcohol, leaving only a slight residue of silica (less than 1 per cent.). On heating, it sublimed in white needles, gave the carbamine reaction when heated with chloroform and alcoholic potash, and possessed all the other properties of aniline hydrochloride.

On analysis—

0·554 gram of substance gave 0 0054 gram of silica and 0·6079 gram of AgCl.

	Found.	Calculated for $C_6H_5 \cdot NH_2,HCl$.
Chlorine	27·14	27 41

The platinochloride separated from solution on the addition of alcohol in small, yellow needles.

On analysis—

0 3925 gram of substance gave 0·1265 gram of platinum.

	Found.	Calculated for $(C_6H_7N)_2,H_2PtCl_6$.
Platinum...........	32·23	32·86

The compound was, therefore, aniline hydrochloride. In order to ascertain how much of this was formed, the precipitate in one experiment, after careful washing, was dried and weighed. It was thus found that half of the aniline, that is. 2 out of the 4 mols. required for 1 mol. of silicon tetrachloride, had been converted into the hydrochloride:—

10·2 grams of aniline yielded 6·7 grams of hydrochloride. Calculated 7 grams.

The filtrate from the aniline hydrochloride was evaporated in a vacuum over sulphuric acid, and left a thick, viscous liquid, which, on being exposed in a desiccator on a porous plate for some days, solidified to a nearly white, amorphous mass. In the dry state, it is almost insoluble in benzene, and all attempts to crystallise it from other solvents were unsuccessful.

The data already given as to the relative amounts of the substances used, and of the hydrochloride of the base formed, indicate the course of the reaction very clearly, and it was therefore only necessary to determine the percentages of two of the constituents, viz., the silicon and chlorine, in order to establish the composition of the compound formed.

The method of analysis adopted depends on the fact that the compound is readily decomposed by water, silica and aniline hydrochloride being formed. The silicon and chlorine can, therefore, both be determined in one portion of the substance in the following way:—

About 0·5 gram of the substance is weighed out into a beaker and treated with water; the greater portion of the silica is thus precipitated, but the remainder goes into solution as soluble silicic acid. The solution is filtered, and the precipitate, after having been well washed with hot water, is ignited and weighed as silica.

In the filtrate, the hydrochloric acid is precipitated with silver nitrate, and the silver chloride collected, washed, and weighed as usual. The filtrate from the silver chloride is then treated with sufficient hydrochloric acid to remove the excess of silver, filtered, and the filtrate evaporated to dryness with strong hydrochloric acid on the water-bath. The residue is moistened with hydrochloric acid, and the insoluble silica collected, washed, ignited, and weighed in the usual way, the weight being added to that of the first precipitate.

The silicon may be more readily determined by decomposing a weighed portion of the compound with water in a platinum crucible, evaporating to dryness with an excess of acid on the water-bath, igniting and weighing as silica. The results obtained in this way agree extremely well with those given by the other method.

The aniline compound gave the following analytical results:—

I. 0·6386 gram of substance gave 0·1262 gram SiO_2 and 0·6281 gram AgCl.

II. 0·5210 gram of substance gave 0·1062 gram SiO_2.

	Found.		Calculated for $SiCl_2(NHC_6H_5)_2$.
	I.	II.	
Silicon	9·01	9·51	9·90
Chlorine	24·28	—	25·03

The formula of the compound is therefore $SiCl_2(NH{\cdot}C_6H_5)_2$, and the reaction by which it is formed is expressed by the following equation:—

$$SiCl_4 + 4C_6H_5{\cdot}NH_2 = SiCl_2(NH{\cdot}C_6H_5)_2 + 2C_6H_5{\cdot}NH_2,HCl.$$

The difficulty of obtaining this compound (and its homologues) in a state of purity is much increased by the circumstance that the viscous liquid left on the evaporation of the benzene solution solidifies gradually in crusts which have to be removed from time to time. Exposure to the air for a short period is necessary for this purpose, and, consequently, absorption of moisture takes place. The decomposition effected by water is expressed by the following equation:—

$$SiCl_2(NH{\cdot}C_6H_5)_2 + 2H_2O = SiO_2 + 2C_6H_5{\cdot}NH_2,HCl.$$

Cold water decomposes the compound quietly, but hot water produces a violent reaction.

The dry compound does not melt when heated, but decomposes, leaving a blackened residue containing a large amount of silicon (about 14 per cent.).

Several analogous substances, which closely resemble the aniline compound in their properties, have been prepared by the action of silicon tetrachloride on various primary aromatic amido-compounds; they have all been obtained and analysed by the methods just described.

Dichlorosilicon-orthoditolyldiamide, $SiCl_2(NH \cdot C_7H_7)_2$.

This compound was obtained by adding an excess of silicon tetrachloride to orthotoluidine, the method described for the preparation of the aniline compound being followed in every particular.

7·3 grams of orthotoluidine required 3·4 grams of silicon tetrachloride. Calculated 2·9 grams.

The precipitate was a white, granular powder, and after washing and drying weighed 5·1 grams. Calculated 4·9 grams. On analysis—

0·6953 gram gave a trace of silica and 0·6833 gram AgCl.

	Found.	Calculated for $C_7H_9N \cdot HCl$.
Chlorine	24·26	24·69

The compound was, therefore, toluidine hydrochloride.

The solution on evaporation in a vacuum yielded the silicon compound, which resembles the aniline-derivative in every respect. It gave the following analytical results:—

I. 0·6348 gram of substance gave 0·1208 gram SiO_2.
II. 0·4130 gram of substance gave 0·0752 gram SiO_2 and 0·3954 gram AgCl.

	Found.		Calculated for
	I.	II.	$SiCl_2(NHC_7H_7)_2$.
Silicon	8·88	8·50	9·01
Chlorine	—	23·65	22·78

The compound, therefore, has the formula $SiCl_2(NH \cdot C_7H_7)_2$.

Dichlorosilicon-dixylyldiamide, $SiCl_2(NH \cdot C_8H_9)_2$.

An excess of silicon tetrachloride was added as before to 8·6 grams of isoxylidine. The liquid became hot, showing that the reaction had taken place, but no precipitate was produced at first, xylidine hydrochloride being slightly soluble in benzene. On cooling, however, a crystalline precipitate was formed, which, on analysis, proved to be xylidine hydrochloride.

0·435 gram of substance gave 0·3983 gram of AgCl.

	Found.	Calculated for $C_8H_{11}N,HCl$.
Chlorine............	22·60	22·49

The liquid was filtered, and the benzene removed from the filtrate by distillation on the water-bath The addition of anhydrous ether to the liquid residue produced a precipitate, the principal portion of the hydrochloride being thrown down together with a small quantity of the silicon compound. The liquid was again filtered and was then evaporated in a vacuum. The residue obtained in this way, however, was not perfectly pure, but still contained some hydrochloride, as will be seen from the analysis —

0·3520 gram of substance gave 0·0532 gram of SiO_2 and 0·3129 gram of AgCl.

	Found.	Calculated for $SiCl_2(NH{\cdot}C_8H_9)_2$.
Silicon..........	7·05	8·27
Chlorine........	21·97	20·89

The compound resembled the aniline-derivative in all its properties.

Dichlorosilicon-β-dinaphthyldiamide, $SiCl_2(NH{\cdot}C_{10}H_7)_2$.

About 8 grams of β-naphthylamine, dissolved in a large quantity of benzene, were treated with an excess of silicon tetrachloride. An exceedingly bulky precipitate of the hydrochloride was formed, the whole mass becoming semi-solid and proving extremely difficult to filter. The filtrate was evaporated in the usual manner and yielded the silicon compound as a white, or slightly pink powder, no viscous liquid being formed; the compound, therefore, was obtained in a purer state than any of the preceding.

It gave the following analytical results:—

0·1990 gram of substance gave 0·0263 gram of SiO_2 and 0·1478 gram of AgCl.

A determination of nitrogen by Dumas's absolute method gave the following numbers:—

0·3865 gram of substance gave 22·1 c.c. of nitrogen measured at 759·1 mm. and 17°.

	Found.	Calculated for $SiCl_2(NH\cdot C_{10}H_7)_2$.
Silicon	7·32	7·31
Chlorine	18·33	18·49
Nitrogen	7·47	7·31

On heating, it decomposed, without melting, in the same manner as the aniline compound.

Several experiments were also made to ascertain the action of silicon tetrachloride on the secondary amines. For this purpose, an excess of silicon tetrachloride was added to a solution of diphenylamine in benzene. No heating effect was noticeable, but after standing for some time a small quantity of a white crystalline deposit was formed. On analysis, this proved to be diphenylamine hydrochloride:—

0·3262 gram of substance gave 0·001 gram of SiO_2 and 0·227 gram of AgCl.

	Found.	Calculated for $(C_6H_5)_2NH,HCl$.
Chlorine	17·18	17·24

The silicon compound, however, could not be obtained in the pure state. Another preparation was made, ether being used instead of benzene, but with the same lack of success.

The action of silicon tetrachloride on the tertiary bases, such as quinoline and pyridine, is of quite a different nature to the foregoing. When the chloride is added to quinoline, immediate combination takes place, accompanied as in the previous cases by a considerable development of heat, and the whole solidifies to a white amorphous mass. After washing with chloroform, the substance smells strongly of the tetrachloride, and loses a considerable portion of this on exposure to the air or on drying in a vacuum. The same result is obtained by heating the mixture in a sealed tube at 100°.

A similar reaction occurs in the case of pyridine. On adding the silicon tetrachloride gradually to pyridine diluted with benzene, it was found that 1 mol. of the chloride was required for 2 mols. of pyridine.

11·7 grams of pyridine required 12 grams of $SiCl_4$. Calculated 12·5.

The filtrate from the dense white precipitate formed contained no silicon.

These compounds lose silicon tetrachloride when gently heated, whilst, when more strongly heated, further decomposition takes place, and a charred residue containing silicon is left. All these properties point to the fact that these substances are simply double compounds containing 1 mol. of silicon tetrachloride to 2 mols. of the base. The analyses show that from one-fifth to one-third of the silicon tetrachloride has been lost in drying. Both the compounds absorb moisture very readily, silica and the hydrochloride of the base being formed.

Pyridine Siliconchloride, $2C_5H_5N,SiCl_4$.

This compound, which is prepared as described above, is a white amorphous powder, which rapidly loses silicon tetrachloride in the air. On analysis—

(I.) 0·7802 gram substance gave 0·1175 gram of SiO_2.
0·916 „ „ 1·2902 „ AgCl.
(II.) 0·5355 gram substance gave 0·0697 gram SiO_2 and 0·7018 gram AgCl.

	Found.		
	I.	II.	Calculated for $2C_5H_5N,SiCl_4$.
Silicon	7·03	6·07	8·53
Chlorine......	34·75	32·35	43·29

The fact that these compounds are derived from the double compound by loss of silicon tetrachloride, is shown by the practical identity of the ratio of the chlorine to the silicon in the three cases:—

	I.	II.	Calculated.
Ratio of Cl to Si	4·94	5·33	5·07

Quinoline Siliconchloride, $2C_9H_7,SiCl_4$.

This compound is formed in a similar manner to the preceding, but is much less stable. It loses silicon tetrachloride so readily and absorbs moisture so eagerly that satisfactory analyses could not be made. On decomposition with water, it forms quinoline hydrochloride and silica. This was proved by treating a portion with water, filtering from the precipitated silica, converting into the platinochloride, and analysing the latter:—

(I.) 0·1953 gram of Pt salt gave 0·0543 gram of Pt.
(II.) 0·4970 „ „ 0·0255 gram H_2O and 0·1380 gram of Pt.

	Found.		
	I.	II.	Calculated for $(C_9H_7N)_2,H_2PtCl_6 + 2H_2O$.
Water	—	5·13	5·11
Platinum........	27·80	27·76	27·82

I propose to continue these investigations, employing the fatty amines for those of the aromatic series, and to endeavour to obtain analogous compounds from the elements allied to silicon.

V.—*Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide.*

By EDWARD DIVERS and TAMEMASA HAGA.

THE solution of an alkali nitrate, saturated with hydrogen sulphide, and then acidified with hydrochloric or sulphuric acid, yields sulphur, nitric oxide, and ammonia, but no hydroxylamine,[*] the presence of this being incompatible with that of what is known as *free* nitrous acid. When the escaping gases are collected out of contact with air, they slowly deposit sulphur, and do so more quickly on bubbling through water into the air, in consequence of reactions between hydrogen sulphide, nitric oxide, and oxygen, but still no hydroxylamine appears.

When, however, *silver nitrite* suspended in water is treated with hydrogen sulphide, besides the sulphur, nitric oxide, and ammonia, still abundantly formed, and the silver sulphide, a considerable quantity of hydroxylamine is also produced. On filtering off the silver sulphide, adding hydrochloric acid to convert the hydrosulphides into hydrochlorides, and evaporating to dryness, a mixture of ammonium and hydroxyammonium chlorides is obtained. Heating the filtrate without first adding an acid causes destruction of the hydroxylamine by the hydrogen sulphide.

---

[*] NOTE BY EDWARD DIVERS *on the dropping the "l" out of the word hydroxylamine.*—It seemed to me unnecessary to urge anything in justification of my action when I ventured to use the spelling, hydroxyamine, in a paper which appeared in the Society's Journal, Trans., 1885, 597; but the Editor's note attached to that paper having shown me my mistake, I now make good the omission. If, as is certainly the case, the composite names in use in chemistry should convey their significance equally to the ear as to the eye, then it seems much better to call oxyammonia *hydrox'yamine* or *hydrox'amine* than to call it *hydroxyl'amine*, and thus avoid accenting an insignificant syllable. It is true that *meth'ylamine*, *phen'ylamine*, and the like, are also commonly pronounced *methyl'amine*, *phenyl'amine*, but there is no difficulty in giving these words their correct and useful sounds, whereas although the pronunciation *hydrox'ylamine* is not an impossible one, the "l" in it proves unpleasantly *de trop*. As we say *hydroxyacetic acid* for *oxyacetic acid*, and similarly throughout the series of hydroxyl compounds, so should we say *hydroxyamine* for *oxyammonia*. Already we do say *hydroxyammonium*, and *hydroxamic acids*. Then, again, we say *nitrosamines*, and not *nitrosylamines*. There is another advantage in dropping the "l," for by doing so the chance is avoided of confounding the last syllable of *oxyl* with the first one of *xylene*, as in *nitroxylene*. (*Cf.* A. H. Allen, *Chem. News*, 54, 83.)

[The term "hydroxylamine" is one which occurs in every text-book and manual, is universally employed by chemists, and is applied to a compound very generally used by those engaged in organic research. There appears to be no reason why we should discard this name, and adopt a *new word* to designate this well-known substance. I may point out that the argument adduced by Dr. Divers, in this note, in favour of dropping the "l" from "hydroxylamine" applies with equal force to methylamine, ethylamine, benzylamine, &c., which would become *methyamine*, *ethyamine*, and *benzyamine* respectively.—THE EDITOR.]

Two estimations were made of the quantity of hydroxylamine in the solution after this had been heated with hydrochloric acid. Silver nitrite, 0·6926 gram, was found, by titration with iodine, to have yielded about one-sixth of its nitrogen as hydroxylamine, whilst in another case, 0·0644 gram yielded as much as three-elevenths of its nitrogen in this form.

In the Society's *Abstracts of Proceedings*, p. 95, there is a preliminary note by us on the reaction between mercurous nitrate and nitric oxide and between mercurous nitrate and alkali nitrites, in which the formation of hydroxylamine is described, together with separation of metallic mercury, and some yellow prismatic crystals of undetermined nature. Soon afterwards one of us succeeded in getting the supposed non-existent *mercurous nitrite*, and this we then identified with our yellow prisms found in the reactions just referred to. Unavoidable delay in completing the examination of mercury nitrites has caused us to put off publishing this paper until now; it is expected that that on mercury nitrites will soon be ready.

Mercurous nitrite yields just the same products as silver nitrite when it is treated with hydrogen sulphide; but as this salt occurs in hard crystals, and is exceedingly insoluble in water, it is difficult to decompose it completely by soluble chlorides including even hydrochloric acid. Accordingly, it resists decomposition by hydrogen sulphide for a long time, and when what appears to be mercury sulphide (and sulphur) is boiled with water, a nitrous odour is observed and mercury goes into solution, due no doubt to the decomposition of some residual nitrite.

It was to the above reaction between mercurous nitrite and hydrogen sulphide that the formation of hydroxylamine was due, when we treated mercurous nitrate first with nitric oxide or alkali nitrite, and then with hydrogen sulphide—mercury nitrite being formed in the reaction we were investigating, and hydroxylamine only by the hydrogen sulphide reducing this nitrite. We cannot indeed affirm positively that hydroxylamine is absent from the mercurial solution before hydrogen sulphide is added, because it is not easy to find a reagent capable of precipitating the mercury—*mercuric* as well as *mercurous*—without decomposing any hydroxylamine that might be present. As we know, however, that nitrite is present in abundance dissolved in the acid mercury solution,* and as this would certainly give hydroxylamine with hydrogen sulphide, whilst the production of this base from mercurous nitrate and nitric oxide alone is most improbable, there is now no ground whatever for believing that it is thus formed.

---

* Evidence of this will be submitted in our forthcoming paper on *mercury nitrites*, together with an account of the formation of the nitrite, and the precipitation of the metallic mercury.

On leaving metallic copper in contact with silver nitrite in water, a bluish-green solution is obtained, from which a little hydroxylamine can be formed by treating it with hydrogen sulphide. A much larger yield can be got from the green mixture of solutions of copper sulphate and potassium nitrite.

From the account we have given of the behaviour of hydrogen sulphide towards nitrites, it may be seen that those nitrites of which the metals—mercury, silver, copper—have especially well marked affinities for nitrogen, and which therefore have a certain stability in presence of acids, are capable of being reduced to hydroxylamine. In great part, indeed, even these nitrites are decomposed by the hydrogen sulphide in such a way as to yield merely the products of the decomposition of this acid by water and additional hydrogen sulphide; but the rest appears to react as follows:—

$$AgNO_2 + 2H_2S = AgNH{\cdot}OH + H_2O + 2S;$$
$$2AgNH{\cdot}OH + H_2S = 2NH_2{\cdot}OH + Ag_2S.$$

As a means of preparing hydroxylamine, the action of hydrogen sulphide on a nitrite has no apparent value. The interest of it lies in the light it may help to throw on the constitution of the oxygen compounds of nitrogen. Experiments made in our laboratory, and already published in the Society's Journal, serve to show that the metals of the zinc-tin class convert nitric acid into ammonia, and not hydroxylamine, when no other acid is present; and into hydroxylamine without ammonia, when acting in conjunction with hydrochloric or sulphuric acid (Trans., 1885, 615), and further, that in the conversion of nitric acid to hydroxylamine, no nitrous acid, nitric peroxide, or nitric oxide, shows itself as an intermediate product (Trans., 1883, 461, 462). An alkali nitrite brought suddenly in contact with hydrochloric acid and zinc sometimes yields a little hydroxylamine (Trans., 1883, 454), but, as pointed out, the probable conversion of the nitrous acid into nitric acid and nitric oxide before it comes in contact with the zinc, leaves the point doubtful whether the little hydroxylamine obtained does not come from nitric instead of from nitrous acid. Thus, it has been left uncertain whether an inorganic nitrite could be converted into hydroxylamine. By the reaction of the nitrites of the silver class of metals with hydrogen sulphide, this uncertainty is at length removed.

In connection with the subject of this paper, it is of interest to consider the well-known behaviour of the nitrohydrocarbons. The application of reducing agents, if appropriate, converts them to amines, but never to hydroxylamines. And yet the paraffin members of the series yield simple or substituted hydroxylamines by appropriate treatment. Plainly, it must be impossible by simple reduction to convert the nitro-compound into the corresponding oximido-compound, because of the difference in valency between the nitroxy- and oximido-radicles; the reaction therefore proceeds probably as follows:—

$$\mathrm{EtN}\triangleleft\mathrm{O_2} + 2\mathrm{H} = \mathrm{EtN(OH)_2},$$
$$\mathrm{EtN(OH)_2} + 4\mathrm{H} = \mathrm{EtNH_2} + 2\mathrm{OH_2}.$$

But when, under special conditions, the hydrocarbon radicle is made to undergo change, it becomes possible to form an oximido-compound (Kissler), or at least hydroxylamine itself (V. Meyer). In these cases, the hydrocarbon acts as the reducing agent on the nitroxyl. Thus, nitroethane at 140°, and in presence of water and hydrochloric acid, yields hydroxylamine, passing probably through the following stage:—

$$\mathrm{MeC}\left\{\begin{matrix}\mathrm{H_2} \\ \mathrm{NO_2}\end{matrix}\right. + \left.\begin{matrix}\mathrm{O_2N} \\ \mathrm{H_2}\end{matrix}\right\}\mathrm{CMe} = \mathrm{MeC}\left\{\begin{matrix}\mathrm{O} \\ \mathrm{NHOH}\end{matrix}\right. + \left.\begin{matrix}\mathrm{HOHN} \\ \mathrm{O}\end{matrix}\right\}\mathrm{CMe}.$$

in which acethydroxamic acid results from the interaction of 2 mols. of the nitroethane, and then, as usual under the circumstances, suffers hydrolysis into hydroxylamine and acetic acid. Again, by the interaction of sodium nitroethane and benzoic or acetic chloride, diacethydroxamic acid is actually obtained as the end-product:—

$$2\mathrm{MeCNaHNO_2} + 2\mathrm{BzCl} = \mathrm{(MeCO)_2NOH} + \mathrm{Bz_2NOH} + 2\mathrm{NaCl}.$$

In this case, each oximido-radicle finds ready for it two univalent radicles in place of the one united to the nitroxyl, in consequence of the elimination of the sodium and chlorine as sodium chloride.

It is thus seen that, under suitable conditions, both nitrites of the metals and organic nitrites (nitronites) reduce to hydroxylamines. It is further seen that the conversion of inorganic nitrites to hydroxylamine lends no support to the view that they have an oxylic constitution, because organic nitrites, beyond doubt non-oxylic, also reduce to oximido-compounds.

VI—*On Morindin and Morindon.*

By T. E. THORPE, F.R.S., and T. H. GREENALL.

THE roots of various species of Morinda, particularly *M. citrifolia* and *M. tinctoria*, are extensively employed in various parts of India, under the general trade name of *Suranji*, as a dye-stuff, more especially for dyeing reds, purples, and chocolates. These plants are to be met with in nearly all the provinces of India, either wild. as in the jungles of Bengal, or cultivated in small patches in betel-nut plantations, or near the homesteads of the dyers.

In Bengal, the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of some 5 or 6 feet, that is, as a rule, at about the end of the third year, the straight spindle-shaped roots, which extend into the ground to a depth of 3 or 4 feet, are dug out, and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root-bark, and is developed in greatest quantities at about the end of three or four years, depending upon the character of the soil. After this time, the dyeing-matter gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are the most valuable, roots thicker than half an inch being thrown away as worthless.

A'l, or Aích, as the root is called in Bengal, is mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but it is also occasionally employed for dyeing the coarse cotton fabric called "Khárua," or for dyeing the silk thread which forms the border of the silk fabric known as "Endi" cloth. The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown-red. The tint seems primarily to depend upon the age of the root, and upon the proportion of root-bark to root-stem which is employed. The root-bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark the resulting dye is reddish-yellow. The methods of A'l-dyeing differ considerably in various parts of India. The usual plan in Bengal is to steep the cloth or yarn in a mixture of powdered castor-oil seeds and the ashes of plantain leaves or other alkaline ashes and water, for some days with alternate washing and drying, after which it is boiled with the dyeing solution prepared by treating the pounded roots, or sometimes the root-bark only with water.

Myrabolans, turmeric, the bark or leaves of *Symplocos racemosa*, alum, certain gums, and various other substances are occasionally used as mordants or auxiliaries either immediately after the cleansing process or along with the dye-stuff; frequently, however, the cloth is transferred directly from the cleansing liquor to the decoction of the root, and no mordant is employed. Purple and chocolates are obtained by adding sulphate of iron to the dyeing liquor.*

It will be observed that this process bears considerable resemblance in its main features to that of Turkey-red dyeing by means of madder, and it is not surprising therefore that some attempts should have been made to introduce *Suranji* into this country as a substitute for the roots of *Rubia tinctorum*. *Morinda citrifolia*, indeed, belongs to the same natural order as the madder plant. The trials made nearly half-a-century ago by Turkey-red dyers in the neighbourhood of Glasgow, to make use of *Suranji* as a dye-stuff were, however, without success.

The first inquiry into the nature of the colouring matters of A'l was made by the late Dr. Anderson (*Trans. Roy. Soc. Edin.*, **16**, iv; *Annalen*, **71**, 216). Anderson found that on boiling the powdered root-bark with alcohol a deep brownish-red solution was obtained, which on cooling deposited the greater part of the colouring matter in brown flocks, mixed with a small quantity of a red substance which was not further examined. By repeated crystallisation from dilute alcohol (50 per cent.), the admixed red substance was removed, and the main product, which Anderson named *morindin*, was obtained in fine needle-shaped lustrous crystals of a yellow or orange-yellow colour. On analysis they gave numbers from which Anderson deduced the formula $C_{28}H_{30}O_{15}$.

On heating morindin in closed tubes, it fused to a deep brown liquid; this at a higher temperature decomposed with the formation of an orange-coloured vapour which condensed to long red needle-shaped crystals, leaving a residue of light porous charcoal. This crystalline product was termed *morindon* by Anderson. The crystals were insoluble in both hot and cold water, but readily soluble in alcohol and ether. Caustic alkalis and also strong sulphuric acid dissolved them with the production of an intense violet colour. With alum, an ammoniacal solution gave a beautiful red lake, and with baryta-water a cobalt-blue precipitate. Anderson's analytical numbers obtained from confessedly imperfectly purified material, led him to express the composition of morindin by the formula $C_{28}H_{20}O_{10}$.

---

* For further details, *see* Liotard "On Indian Dyes;" also McCann, "Dyes and Tans of Bengal."

Hence it might be assumed to be derived from morindin by the elimination of 5 mols. of water, a view of its origin which Anderson held to be substantiated by the mode of action of oil of vitriol upon morindin. After treatment with the acid, the solution of morindin gave on dilution with water a yellow flocculent precipitate, insoluble in water, but soluble in alkalis with the violet colour characteristic of morindon.

According to Rochleder (*Wien. Akad. Ber.*, 7, 806), Anderson's morindin is probably identical with ruberythric acid, $C_{26}H_{28}O_{14}$, the formula of which agrees practically as well with Anderson's analytical numbers as that which he himself deduced from them. Hence, therefore, morindon would probably be identical with alizarin, to which, indeed, from Anderson's description of its physical properties, it bears considerable resemblance. This view of the nature and relation of morindin and morindon was supported by Stenhouse (*Chem. Soc. J.* [1864], 17, 333), mainly from a comparison of the absorption spectra of morindon and alizarin. It would appear, therefore, that the colouring matters of A'l and of madder were probably identical.

Several facts, however, seem to be inconsistent with this supposition. We have first the circumstance of the inability of the Glasgow dyers to procure madder colours from *Suranji*. Anderson, also, was unable to obtain more than a brownish-red colour in a trial of the Turkey-red process with pure morindin. Morindon, on the other hand, he found to combine readily with mordants, giving with alumina a deep rose-red, and a violet or black colour with oxide of iron. Stein also (*J. pr. Chem.*, 97, 234) has adduced evidence to show that Anderson's morindin is not identical with ruberythric acid, and that morindon is not identical with alizarin. According to Stein, morindin is distinguished from ruberythric acid by its insolubility in ether, by the violet colour of its barium-compound, and by its behaviour with caustic potash. It is, like ruberythric acid, a glucoside, and by heating alone, or by the action of alkalis, is converted into products which reduce an alkaline solution of copper oxide. It melts at 245°, but even below this temperature it gives a crystalline sublimate of morindon.

Stein found that the readiest way of preparing morindon was to hydrolyse a dilute alcoholic solution of morindin with hydrochloric acid, when the greater part of the morindon is deposited, on cooling, as a bright reddish-yellow flocculent precipitate. In this manner morindin yields about half its weight of morindon, whereas ruberythric acid if decomposed in accordance with the equation $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$, gives only 42·5 per cent. of alizarin.

Morindin dissolves in oil of vitriol, forming a solution which is at first indigo-blue, but this gradually changes to a reddish-purple, and eventually becomes yellowish-red. Alizarin gives a reddish-purple coloured solution at once. With ferric chloride, an alcoholic solution of morindon gives a dull green colour, whereas with alizarin the colour is reddish-brown. When oxidised with nitric acid, morindon gives no phthalic acid but only oxalic acid. According to Anderson (*loc. cit.*), however, the nitric acid solution of morindon, after long continued boiling and subsequent neutralisation with ammonia, gives no precipitate with salts of lime. Stein found that the optical behaviour of solutions of morindon agreed perfectly with the description given by Stokes, and on which Stenhouse based his assumption of the identity of morindon and alizarin.

This conflict of testimony respecting the real nature of the colouring matter of A'l seemed to warrant fresh investigation. Thanks to the kindness of the Director of the Royal Gardens, Kew, who was good enough to make application to the India Office on our behalf, we obtained about 10 lbs. of the roots of *M. citrifolia.* The method of extraction we employed was substantially that described by Anderson, the powdered root-bark being repeatedly treated with hot dilute alcohol so long as anything seemed to be dissolved. The roots as received from the India Office were in two parcels, the one parcel consisting of thick and evidently old roots, the other of thin roots as a rule not more than ¼ inch thick: these alone appeared to contain any sensible quantity of the colouring matter. The alcoholic extracts were concentrated by evaporation, and the precipitates which formed on standing, were collected and treated first with benzene, and then with absolute alcohol, so long as any red colouring matter passed into solution. The residue was then dissolved in hot 50 per cent. alcohol, and purified by repeated crystallisation. In this manner about a gram of pure morindin was obtained. After being dried at 100°, it yielded the following numbers on analysis:—

I. 0·2024 gram gave 0·4098 gram CO_2 and 0·0930 gram H_2O.
II. 0·2088 " 0·4236 " " 0·0951 "

	Calculated for $C_{26}H_{28}O_{14}$ (rubererythric acid).	Calculated for $C_{28}H_{30}O_{15}$.	Anderson's analysis.	I.	II.
C......	55·33	55·44	55·43	55·27	55·37
H	4·96	4·95	5·11	5·11	5·06
O......	39·71	39·60	—	—	—
	100·00	100·00			

It will be observed that our analytical results are in close agreement with those of Anderson, and that both sets of numbers are almost as well expressed by the formula $C_{28}H_{30}O_{15}$ as by that of ruberythric acid.

Through the kindness of Dr. Schunck, who forwarded us a specimen of ruberythric acid, we have been enabled to make a comparison of the properties and modes of decomposition of that substance with those of morindin. In appearance, the two substances were almost exactly similar. When heated in capillary tubes placed side by side, they both decomposed with charring at about the same temperature, and yielded reddish or violet vapours condensing to crystalline sublimates. Contrary to the statements of Rochleder and Stein, ruberythric acid was found to be practically insoluble in ether. Ruberythric acid and morindin are however at once distinguished by their reaction with potash: both give bright red solutions, but, on boiling, that of ruberythric acid at once changes to a dark purple, whilst that of morindin does not alter even after long-continued boiling: this reaction is very striking and characteristic.

A further proof that ruberythric acid and morindin are not identical is afforded by their behaviour on hydrolysis. 0·4354 gram ruberythric acid and 0·4884 gram morindin were separately dissolved in 80 c.c. boiling 50 per cent. alcohol together with 8 c.c. strong hydrochloric acid solution. The solutions were heated by steam under a reflux condenser for about four hours, when the hydrolysis was found to be complete. The precipitates were then collected, washed with water, dried at 120°, and weighed. The weights were—

From ruberythric acid, 0·1832 gram = 42·1 per cent.
" morindin " 0·2369 " = 48·5 "

The proportion of the hydrolysed product to the morindin employed agrees closely with the result obtained by Stein: the amount of the hydrolysed product in the case of the ruberythric acid is nearly 6½ per cent. lower, and is almost identical with that required by the equation $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6$, which gives 42·5 per cent. of alizarin.

Moreover the two products behaved very differently towards reagents. That from ruberythric acid gave a blue-purple colour with potash, unchanged on standing; in the case of that from morindin, the colour was reddish-purple and gradually faded. With ferric chloride, the ruberythric acid product gave a dull brownish-yellow coloration; with the morindin product, the colour was sage-green. With concentrated sulphuric acid, the product from ruberythric acid gave a bright yellowish-red; whereas in the case of the morindin product the coloration was first dark-blue and then purple. Seen under the microscope, the forms of the two products as crystallised from benzene were quite distinct. The two products were then submitted to analysis, after being heated, side by side, at 130°, with the following results :—

Product from ruberythric acid :—

0·1457 gram gave 0·3726 gram CO_2 and 0·0458 gram H_2O.

	Found.	Calculated for alizarin, $C_{14}H_8O_4$.
C........	69·74	70·00
H........	3·49	3·33
O........	26·77	26·67
	100·00	100·00

Product from morindin—

0·1604 gram gave 0·3906 gram CO_2 and 0·0554 gram H_2O.

	Found.	Calculated for trihydroxymethylanthraquinone, $C_{15}H_{10}O_5$.	Calculated for isopurpurin, $C_{14}H_8O_5$.
C......	66·41	66·66	65·62
H......	3·83	3·70	3·12
O......	29·76	29·64	31·26
	100·00	100·00	100·00

There would seem therefore to be no doubt that morindin and ruberythric acid are not identical as was supposed by Rochleder and Stenhouse. The true nature of morindon has still to be determined; the amount of material at our disposal was unfortunately insufficient for its further investigation. In many of its reactions morindon closely resembles isopurpurin, although the numbers afforded by its analysis agree more nearly with those required by trihydroxymethylanthraquinone. In either case, its formation by hydrolysis is not very readily explained. We made attempts to determine the quantity of sugar yielded by the decomposition of a known weight of the morindon, but the amount obtained (35 per cent.) threw no light upon the mode in which the morindin is derived, or upon its probable formula. It is, however, quite certain that morindin is not identical with the only trihydroxymethylanthraquinone at present known, viz., the *Emodin* discovered by Warren De la Rue and Hugo Müller in rhubarb root (*Chem. Soc. J.*, **10**, 304). Our thanks are due to Dr. Hugo Müller for his kindness in affording us the opportunity of comparing the properties of the two products. Since the experimental work in connection with this communication was concluded, Mr. Thomas Wardle, of Leek, has kindly placed a quantity of the roots of *M. citrifolia* and *M. tinctoria* at our disposal. As, however, we are unable to prosecute the work in common any further, we have ventured to bring the results obtained up to now before the Society. One of us hopes to be shortly in a position to present the results of a fuller investigation.

A portion of the work was done in the laboratory of the Yorkshire College: our thanks are due to Mr. C. W. Gamble, a former student of that institution, for his assistance in the extraction of the crude colouring matter from the roots.

VII.—*Spectroscopic Notes on the Carbohydrates and Albuminoïds from Grain.*

By W. N. Hartley, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

According to C. v. Nägeli ("*Theorie du Gährung*"), fermentation is a process which may be described as the transference to fermentable matter of the molecular or rather intramolecular vibrations of the different constituent substances entering into the composition of living protoplasm (which remains itself unchanged in composition), and hence the equilibrium of the molecules of the fermentable matter becomes so disturbed as to cause their resolution into simpler molecules. In this case, the intramolecular vibrations of the substances are transferred through the cell-wall of the *saccharomyces* to the molecules of sugar outside. It appears by no means improbable that the diastatic ferments may have some such action; therefore any facts bearing on this matter are of interest. The vibrations of the active substances must be either of greater amplitude than those of the carbohydrates, or else of much greater frequency; for if of the same frequency but of lesser amplitude they could not cause any such effect as that described.

Now it seemed to me to be possible to learn something of the mode and rate of vibration both of the molecules of the carbohydrates and of the diastatic ferments. Accordingly I have photographed the absorption spectra transmitted by solutions of saccharose, glucose, and starch, as also those of several albuminoid compounds and egg-albumin. For specimens of diastase from malt and invertase from yeast, I am indebted to Mr. Cornelius O'Sullivan, who kindly placed specimens at my disposal some two years and a half since, with the offer of a further supply if necessary.

While the work was in progress, M. L. Soret published his fifth memoir on the absorption of ultra-violet rays by different substances, which included an examination of the various forms of albumin (*Archives des Sciences Physiques et Naturelles*, **10**, 139; *Compt. rend.*, **97**, 642), the carbohydrates, glucose, saccharose, and gelatin. My results proved to be in strict agreement with his as regards these substances; it is proposed, therefore, to give them in abstract only. Considerable difficulty was encountered in photographing some of the liquids on account of their opalescence, which prevented more than thin layers of liquid from being examined. In one or two cases, as with gelatin and with starch, the liquid was allowed to dry on plates of quartz, and the rays were passed through the dried films. This proved decidedly advantageous, but on the whole the turbidity of the solutions has been a source of much trouble.

Gelatin.—(1.) A yellow specimen sold for photographic purposes, said to be of Nelson's preparation, but without any distinctive label. A solution containing 5 per cent. of the solid and 1 mm. in thickness was allowed to dry on a plate of quartz. It transmitted a continuous spectrum to wave-length 2265, but beyond 2313 the rays were weak.

(2.) A very fine colourless sample made in sheets, which in the original form transmitted all rays to 2265. A solution containing 5 per cent. and 1 mm. in thickness, dried on a plate of quartz, transmitted all rays to wave-length 2265 in full intensity.

Maize Starch.—Brown and Polson's corn flour. A solution of 1 part to 12 of water and 1 mm. thick, dried on a plate of quartz, transmitted a spectrum of normal strength as far as wave-length 2145.

Cane-sugar.—A solution containing 10 per cent. transmits all rays through as much as 25 mm. as far as wave-length 2145. Very highly diactinic.

Glucose.—A very pure specimen. A solution containing 10 per cent. transmits all rays through a thickness of 10 mm. as far as 2145.

Albumin.—White of egg. According to M. Soret's measurements, the following wave-lengths have been reckoned:—

			Absorption-band.
2	mm.	diluted with water twice, from about	2880 to 2650
3½	„	„ five times from ..	„ „
4	„	„ nine times „ ..	„ „

The same absorption-band occurs when albumin is acidified.

Pure Albumin.—When a solution of pure albumin containing 37 grams per litre is examined, 2 mm. of the liquid exhibit an absorption-band from about 2948 to 2572 wave-lengths.

Casein.—A solution containing 6·5 grams per litre. 8 mm. and 9 mm. Absorption-band from about 2948 to 2572.

Serin.—Solution containing 10·5 grams per litre. 4 mm. to 5 mm. A similar band.

Solutions of invertase and diastase were prepared from Mr. O'Sullivan's specimens. Invertase was also prepared from compressed porter yeast by simple treatment with water and filtration, the yeast being from the brewery of Messrs. A. Guinness and Sons. The solutions were difficult to examine, especially the diastase; the considerable quantity of matter dissolved rendered filtration difficult, and they showed a certain degree of turbidity not easily removable. The possibility of manipulating the liquids so as to clarify them was interfered with by reason of the facility with which they putrefy and the necessity of avoiding the addition of any preservative to them. The following is a description of the spectra:—

Invertase.—A solution containing about 1 per cent. or 0·1 gram dissolved in as little water as possible, between 8 c.c. and 10 c.c., and filtered.

	Wave-lengths.	Oscillation frequencies.
20 mm., continuous spectrum to	2418	4136
15 „ „ „	2313	4326
10 „ „ „	2263	4420
5, 4, and 3 mm. continuous spectrum to	2193	4555
2 and 1 mm., continuous spectrum to.	2148	4658

Yeast Water.—The same result was obtained as with invertase.

Diastase.—A solution containing about 1 per cent. or 0·1 gram in 10 c.c. of water. The turbidity of this solution weakened the spectrum throughout when a thickness of 10 mm. was examined.

	Wave-lengths.	Oscillation frequences.
10 mm., 9 mm., and 8 mm., continuous to..................	2988	3359
A strong line faintly visible at..	2568	3890
7 mm. and 6 mm., continuous to	2568	3890

The albuminoïds, invertase and diastase, are evidently of very different constitution from albumin, caseïn, and serin, all of which, as Soret has shown, have something in common, which is disclosed by the absorption-band common to their spectra. Gelatin differs from these forms of albumin. While albumin, caseïn, and serin exhibit absorption-bands in dilute solutions and in small thicknesses of such solutions, gelatin, invertase, diastase, starch, glucose and saccharose, under like circumstances, are seen to be highly diactinic and show no absorption-bands. It does not therefore appear likely that a substance of the character of albumin could affect the carbohydrates, while on the other hand it is possible that the intramolecular vibrations of invertase and diastase might be communicated to saccharose and starch. From this, of course, it follows that there may be in yeast-water or within the yeast-cell some similarly constituted albuminoïd capable of acting on glucose in a manner similar to the action of invertase on saccharose, but yielding different products. Setting aside theoretical considerations touching fermentation, it is of great interest to find that substances of such complex composition as the sugars so extraordinarily diactinic, for this is quite in character with what we know of their constitution. It is no less interesting to learn that the albuminoid compounds associated with the carbohydrates are evidently different in constitution from those forms of albumin found in the animal organism. The probability presents itself of these albuminoids being derived from the carbohydrates. The examination of specimens of gelatin shows that the difficulty in obtaining photographic plates, sensitive to the most refrangible rays, lies entirely with the character of the gelatin. Ordinarily the spectrum extends to wave-length about 2146 Cd. Some plates prepared many years ago by Wratten and Wainwright, called ordinary dry plates, were used for photographing a series of metallic spectra which extend to wave-length 2024 Zn, and there is little doubt that they were capable of receiving impressions of lines still more refrangible. Since then plates of every kind by every maker have been tried, but most of these transmit nothing beyond 2146 Cd. A sample from Mawson and Swan was recently found to photograph as far as 2024, but half a dozen other batches from the same makers were deficient in this respect, notwithstanding that they were supposed to be of exactly the same character. As the plates were prepared in precisely the same way, there can be no doubt that the difference was in the gelatin, which must have contained some very slight trace of impurity which could not otherwise be detected.

VIII.—*The Action of Salicylic Aldehyde on Sodium Succinate in presence of Acetic Anhydride.*

By Gibson Dyson, Ph.D, Demonstrator of Chemistry, Normal School of Science, South Kensington.

In order to see if Perkin's reaction is equally applicable to the hydroxyaldehydes, I undertook, at the request of Professor Fittig, to study the action of salicylic aldehyde on sodium succinate.

Jayne (*Annalen*, 216, 97) has shown that by acting on sodium succinate with benzaldehyde, at a temperature of 100—120°, phenylparaconic acid is principally formed. It was, therefore, to be expected that by substituting salicylic aldehyde for benzaldehyde, hydroxyphenylparaconic acid would be obtained. This was not found to be the case, however, the product being a neutral substance having the composition $C_{18}H_{10}O_4$, which subsequent investigation proved to be dicoumarin. In 1872, Zwenger (*Annalen*, Sup. 8, 32) showed that when coumarin, in aqueous solution, is treated with sodium amalgam, it gives melilotic acid, $C_9H_{10}O_3$: by acting with sodium amalgam on a saturated alcoholic solution of coumarin, however, the reaction proceeded quite differently; in this case he obtained the sodium salt of a new acid, which he called hydrocoumaric acid, $C_{18}H_{18}O_6$. The characteristic properties of this acid are, that its sodium salt is practically insoluble in alcohol, and that on being heated it gives off 2 mols. H_2O, forming an anhydride melting at 222·6°.

Cohen (*Inaugural Dissertation*, München, 1884), by the reduction of β-methylumbelliferon-paramethyl ether in alcoholic solution with sodium amalgam, obtained a compound, $C_{22}H_{22}O_6$, which he regarded as belonging to the same class of compounds as Zwenger's acid. As the substances above mentioned are the only dicoumarins known, it seemed desirable that the dicoumarin obtained by the action of salicylic aldehyde on sodium succinate should be submitted to a thorough investigation.

Preparation of Dicoumarin.

A mixture of salicylic aldehyde, sodium succinate (dried at 140° C.), and acetic anhydride, in the proportions of their respective molecular weights, was heated for 24 hours on the water-bath in a flask connected with a reflux condenser. It is essential to the success of the experiment that every trace of moisture should be excluded from the apparatus, and that all the material used should be perfectly dry. The contents of the flask, which had darkened in colour, were treated with hot water to remove sodium succinate and the acetic anhydride which still remained unacted on; and the excess of salicylic aldehyde was removed by a current of steam. The dicoumarin, after being washed with ether to remove a tarry substance which is always formed in small quantity, remained as a pale-yellow crystalline powder, insoluble in all the ordinary solvents. It was recrystallised from hot glacial acetic acid, in which it is only sparingly soluble; on cooling, it separated out in needle-shaped crystals.

The analysis of this compound indicated the composition $C_{18}H_{10}O_4$; it is formed by the condensation of 2 mols. of salicylic aldehyde with 1 mol. of succinic acid.

As by the above method the greater part of the aldehyde remained unacted on, the following modification was tried, and the results being more satisfactory, it was adopted for the preparation of all the material used in this research.

A mixture of 10 grams of sodium succinate, 15 grams of salicylic aldehyde, and 13 grams of acetic anhydride, was heated in a sealed tube for 40 hours at 140°. The contents of the tube were then extracted with hot water, and the residue, which consists of dicoumarin and unaltered salicylic aldehyde, was treated in exactly the same manner as previously described. From 10 grams of salicylic aldehyde about 5 grams of dicoumarin were obtained. It was found that an excess of acetic anhydride did not increase the yield of dicoumarin, but gave rise to the formation of various complicated condensation products, which have not been further investigated. The dicoumarin was purified by recrystallisation from hot glacial acetic acid; the product thus obtained was slightly yellow, and it was found impossible by this method of purification to render it colourless. It can, however, be completely decolorised by dissolving it in a hot solution of soda, and then reprecipitating it by the addition of hydrochloric acid.

The melting point of dicoumarin lies above 330°. On fusing it with caustic soda, salicylic acid is formed.

The following are the analytical results obtained:—

I. 0·2012 gram of substance gave 0·5552 gram of CO_2 and 0·0650 gram of H_2O.

	Calculated for $C_{18}H_{10}O_4$.	Found.
C	74·48 per cent.	74·84 per cent.
H	3·45 ,,	3·54 ,,

II. Analysis (after being recrystallised). 0·285 gram of substance gave 0·7775 gram of CO_2 and 0·0908 of H_2O.

	Calculated for $C_{18}H_{10}O_4$.	Found.
C	74·48 per cent.	74·40 per cent.
H	3·45 ,,	3·53 ,,

Dicoumarin is an extremely stable compound, insoluble in ether, alcohol, and benzene, but slightly soluble in chloroform and glacial acetic acid; it is not acted on at the ordinary temperature by sodium carbonate, ammonia, or caustic soda. On boiling it for some time with a solution of sodium or barium hydrate, it slowly dissolves, forming a yellow solution from which it is reprecipitated unchanged on addition of an acid.

The following is an analysis of the product thus obtained :—

0·220 gram of substance gave 0·6003 gram of CO_2 and 0·0726 gram of H_2O.

	Calculated for $C_{18}H_{10}O_4$.	Found.
C	74·48 per cent.	74·45 per cent.
H	3·45 „	3·66 „

If, however, hydrochloric acid is gradually added to the alkaline solution, and this is kept cool by means of a freezing mixture, a precipitate is obtained which redissolves on addition of sodium carbonate. On attempting to separate this precipitate by filtration, it is immediately decomposed, dicoumarin being regenerated. It is probable that the compound formed is an unstable oxyacid, similar in fact to that obtained by dissolving dicoumarin in caustic soda.

The formation of dicoumarin from salicylic aldehyde and succinic acid may be represented by the following equation :—

$$2C_6H_4(OH)\cdot CHO + C_4H_6O_4 = C_{18}H_{10}O_4 + 4H_2O.$$

Action of Sodium Amalgam on Dicoumarin.

An alkaline solution of dicoumarin, prepared by dissolving dicoumarin in hot concentrated caustic soda and diluting with water, was treated on the water-bath, with sodium amalgam (containing 5 per cent. of sodium), until the precipitate produced by the addition of hydrochloric acid redissolved completely on adding sodium carbonate.

In order that the reduction may not proceed too slowly, it is necessary to keep the solution as nearly neutral as possible. This is done by the occasional addition of hydrochloric acid. The alkaline liquid was decanted from the mercury, acidified with hydrochloric acid, and the precipitate formed collected on a filter. It is not soluble in chloroform or benzene, and only slightly so in water and ether, but dissolves freely in alcohol; it is also soluble in a solution of sodium carbonate, with evolution of carbon dioxide. It was purified by recrystallisation from dilute alcohol. The product thus obtained was found to have an indefinite composition, and it was, therefore, assumed to be a mixture. Proceeding on this assumption, various methods of separation were tried, and it was finally found that by converting it into the barium salt, and fractionally recrystallising the latter, the pure acid could be obtained. The mixture was accordingly dissolved in a solution of barium hydrate, and the excess of barium precipitated from the hot solution by a current of carbon dioxide. On filtering and allowing the filtrate to cool, a barium salt separated out, having the composition $(C_{18}H_{13}O_5)_2Ba + xH_2O$, being, in fact, barium hydrodicoumarate. In the mother-liquor, there still remained a small quantity of the last-named salt, together with a salt much more easily soluble in water. The latter is undoubtedly the barium salt of the acid obtained by further reduction of hydrodicoumaric acid. It was found that when the reduction of the dicoumarin was only continued until it was all decomposed, very little of this more highly-reduced acid was formed.

Hydrodicoumaric Acid, $C_{18}H_{14}O_5$.

This acid was obtained, as a white precipitate, by adding hydrochloric acid to a solution of the barium salt. It is insoluble in chloroform and benzene, and dissolves only slightly in hot water or ether, but freely in alcohol. By recrystallisation from dilute alcohol, it was obtained in needle-shaped crystals.

When heated at 130°, it loses the elements of water, forming an anhydride, $C_{18}H_{12}O_4$.

Dried over sulphuric acid (when dried at 100° it lost weight, probably due to the formation of a small quantity of the anhydride) it yielded on analysis the following figures:—

0·0215 gram of substance gave 0·5485 gram of CO_2 and 0·0906 gram of H_2O

	Calculated for $C_{18}H_{14}O_5$.	Found.
C	69·67 per cent.	69·58 per cent.
H	4·51 „	4·67 „

Barium Salt, $(C_{18}H_{13}O_5)_2Ba + xH_2O$.

The preparation of this salt has already been described. It is only slightly soluble in cold water, but more readily in hot, from which it separates on cooling in well-defined crystals. These on exposure to the air effloresce and become opaque, rendering it impossible either to determine the water of crystallisation or the crystalline form. The following are the analytical figures obtained:—

I. 0·3861 gram of salt gave on heating at 130° 0·04725 gram of water, and on treatment with sulphuric acid 0·1047 gram of barium sulphate.

	Calculated for the dried salt.	Found.
Ba	18·18 per cent.	18·14 per cent.

The formula $(C_{18}H_{13}O_5)_2Ba + 6H_2O$ requires 12·51 per cent. of water. Found 12·2 per cent.

II. 0·31275 gram of the salt gave 0·05675 gram of water, and on treatment with sulphuric acid 0·0787 gram of barium sulphate.

	Calculated for the dried salt.	Found.
Ba........	18·18 per cent.	18·34 per cent.

Calculated for $(C_{18}H_{13}O_5)Ba + 9H_2O$ = 17·66 per cent. of water. Found 18·14.

Silver Salt, $C_{18}H_{13}O_5Ag$.

On adding silver nitrate to a solution of the barium salt, the silver salt was obtained as a white curdy precipitate, which on standing became crystalline. It is almost insoluble in water. The analysis of the salt, dried over sulphuric acid, gave the following figures :—

0·2325 gram of the salt yielded 0·4427 gram of CO_2, 0·0687 gram of H_2O, and 0·0595 gram of Ag.

	Calculated for $C_{18}H_{13}O_5Ag$.	Found.
C	52·13 per cent.	51·93 per cent.
H	3·12 ,,	3·28 ,,
Ag........	25·82 ,,	25·59 ,,

The calcium salt, obtained by treating the ammonium salt with calcium chloride, is almost insoluble in water.

Hydrodicoumarin, $C_{18}H_{12}O_4$.

Hydrodicoumaric acid, as has already been mentioned, splits up on being treated at 133°, into the anhydride, hydrodicoumarin, and water. In order to prepare hydrodicoumarin, hydrodicoumaric acid, which for the purpose need not be quite pure, is melted between watch-glasses. The melt, on cooling, is first washed with alcohol, in order to remove any unaltered acid, and then dissolved in hot chloroform; on allowing the chloroform to stand, hydrodicoumarin is deposited in small but well-defined crystals. It can also be precipitated directly by the addition of alcohol. Hydrodicoumarin is insoluble in water, alcohol, and ether; it melts at 256°, and when heated above this temperature it sublimes with partial decomposition in needle-shaped crystals; the vapour has an odour resembling that of coumarin.

On analysis, the following numbers were obtained :—

0·2217 gram of the anhydride yielded 0·6028 gram of CO_2 and 0·0833 of H_2O.

	Calculated for $C_{18}H_{12}O_4$.	Found.
C	73·97 per cent.	74·09 per cent.
H	4·11 ,,	4·17 ,,

In order to see if it could easily be reconverted into the acid, it was boiled with water for three days; at the end of which time it was found to be unaltered. It is not attacked when boiled with sodium carbonate or dilute caustic soda, but if heated for some time with a concentrated solution of caustic soda it is reconverted into the acid.

The crystals of hydrodicoumarin obtained from its solution in chloroform were not satisfactory, and it was thought that a better product might be obtained by recrystallising it from dilute acetic acid. Hydrodicoumarin was, therefore, dissolved in hot glacial acetic acid, and water, added until the precipitate formed just redissolved on boiling.

After two crystallisations a well-crystallised substance was obtained, which on analysis gave the following results:—

0·2173 gram of substance gave 0·5581 gram of CO_2 and 0·091 gram of H_2O.

	Calculated for hydrodicoumaric acid, $C_{18}H_4O_5$.	Found.
C	69·97 per cent.	70·00 per cent.
H	4·51 „	4·65 „

From the above result, it would follow that by boiling hydrodicoumarin with acetic acid hydrodicoumaric acid is reformed. I hope to be able to give more details regarding this reaction in my next paper.

Action of Bromine on Hydrodicoumaric Acid.

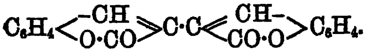
Hydrodicoumaric acid, suspended in chloroform, was treated with the calculated quantity of bromine (2 mols. of Br to 1 mol. of the acid). It is necessary, in order to prevent the formation of substitution products, to keep the mixture cool by surrounding it with ice; if this precaution is taken, no hydrogen bromide is given off. A clear solution was obtained, which after a time deposited a white precipitate; it was impossible, however, to analyse this compound, as on attempting to dry it, it immediately decomposed, giving off hydrogen bromide and leaving a white insoluble substance. This was purified by dissolving it in hot glacial acetic acid, from which on cooling it separates out in crystals. On analysis, the following numbers were obtained:—

0·291 gram of the substance gave 0·1499 gram AgBr.

	Calculated for $C_{16}H_{11}BrO_4$.	Found.
Br	21·56 per cent.	21·92 per cent.

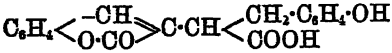
The compound is consequently monobromohydrodicoumarin. It is insoluble in alcohol and ether, and dissolves only slightly in chloroform. In the original solution there still remained a compound, easily soluble in chloroform, which has not yet been analysed.

As dicoumarin is formed by the condensation of 2 mols. of salicylic aldehyde with 1 mol. of succinic acid, it follows that the simplest constitution that can be assigned to it is



$$C_6H_4{<}\begin{matrix}-CH\\O\cdot CO\end{matrix}{>}C\cdot C{<}\begin{matrix}CH-\\CO\cdot O\end{matrix}{>}C_6H_4.$$

It has further been been shown that by limited reduction dicoumarin yields a monobasic acid, to which the constitution



$$C_6H_4{<}\begin{matrix}-CH\\O\cdot CO\end{matrix}{>}C\cdot CH{<}\begin{matrix}CH_2\cdot C_6H_4\cdot OH\\COOH\end{matrix}$$

has been given.

From this it would appear as if it were necessary, in order for the oxyacid to be stable, that the COOH group be combined with a saturated carbon-atom. It was therefore to be expected that, by further reduction of hydrodicoumaric acid, a bibasic acid would be formed, which should be identical with Zwenger's acid.

Action of Sodium Amalgam on Hydrodicoumaric Acid.

Hydrodicoumaric acid was dissolved in a solution of sodium carbonate and treated repeatedly on the water-bath with sodium amalgam (containing 5 per cent. of sodium). The reduction must be continued for several days, and the solution kept as nearly neutral as possible. On decanting the alkaline solution from the mercury, and acidifying with hydrochloric acid, the new acid was obtained as a white precipitate. It can be purified by recrystallisation from water or dilute acetic acid. The best method, however, to obtain it perfectly pure, is to convert it into the calcium salt, which can be purified by recrystallisation from hot water. As the calcium salt of hydrodicoumaric acid is nearly insoluble in the last-named solvent, an easy separation of the two acids can be effected.

The new acid, crystallised from dilute acetic acid, forms colourless crystals soluble in alcohol but insoluble in chloroform. When heated above 100°, it is slowly decomposed, without changing its outward appearance, forming an anhydride. The analysis shows it to have the same composition as Zwenger's hydrocoumaric acid, $C_{18}H_{18}O_6$, with which, however, it is not identical. This acid may be named *dihydrocoumaric acid.* If forms an insoluble silver salt, and a sodium salt soluble in alcohol.

0·2216 gram of the acid yielded 0·5333 gram of CO_2 and 0·1101 gram of H_2O.

	Calculated for $C_{18}H_{18}O_6$.	Found.
C	65·45 per cent.	65·63 per cent.
H	5 45 ,,	5·52 ,,

Calcium Dihydrocoumarate, $C_{18}H_{16}O_6Ca + 6H_2O$.

This salt was prepared by boiling the acid with water containing calcium carbonate in suspension. On filtering from excess of calcium carbonate and concentrating the filtrate, it separated on cooling in radiating groups of acicular crystals, containing 6 mols. H_2O, which it loses at 140°.

I. 0·3084 gram of the salt gave 0·0710 gram of water, and on addition of sulphuric acid 0·0893 gram of calcium sulphate.

	Calculated for $C_{18}H_{16}O_6Ca + 6H_2O$.	Found.
Ca	8·40 per cent.	8·52 per cent.
H_2O	22·69 ,,	23·00 ,,

II. 0·1616 gram of salt gave 0·036 gram of water and 0·0466 gram of calcium sulphate.

	Calculated for $C_{18}H_{16}O_6Ca + 6H_2O$.	Found.
Ca	8·4 per cent.	8·48 per cent.
H_2O	22·69 ,,	22·27 ,,

Silver Salt, $C_{18}H_{16}O_6Ag_2$.

On adding silver nitrate to a solution of the calcium salt (if the ammonium salt be used the product is impure), the silver salt was obtained as a white voluminous precipitate, which on standing became crystalline. The analysis of this salt dried at 100°, gave the following results:—

0·1945 gram of salt yielded 0·2831 gram of CO_2, 0·0578 gram of H_2O, and 0·0768 gram of Ag.

	Calculated for $C_{18}H_{16}O_8Ag_2$.	Found.
Ag........	39·70 per cent.	39·48 per cent.
C	39·70 ,,	39·76 ,,
H	2·96 ,,	3·26 ,,

Second determination of the silver:

0·2377 gram of salt gave 0·0939 gram of Ag.

	Calculated.	Found.
Ag........	39·7 per cent.	39·5 per cent.

Dihydrocoumarin, $C_{18}H_{14}O_4$.

The anhydride was obtained by melting the acid between watch glasses. The melt was then washed with alcohol, in order to remove any undecomposed acid, and dissolved in chloroform; from this solution it separated out on the addition of alcohol, or on standing, in needle-shaped crystals. It melts at 222—224°, and sublimes, with partial decomposition, when heated above this temperature; the vapours have an odour similar to that of coumarin; on boiling with water or carbonate of soda, it is not altered, but when heated with caustic soda it is slowly dissolved, being reconverted into the acid; when it is fused with solid caustic soda, salicylic acid is formed.

The following are the analytical results obtained:—

0·169 gram of the substance gave 0·4554 gram of CO_2 and 0·0734 gram of H_2O.

	Calculated for $C_{18}H_{14}O_4$.	Found.
C	73·47 per cent.	73·49 per cent.
H	4·76 „	4·81 „

The anhydride seems to be identical with that obtained by heating Zwenger's acid, possessing as it does the same chemical composition and melting point.

As the properties of the acid, from which the anhydride was prepared, do not correspond with those given by Zwenger to his acid, it was thought desirable to prepare a specimen of the acid according to his directions.

Preparation of Hydrocoumaric Acid.

20 grams of coumarin were dissolved in about 50 c.c. of absolute alcohol, and treated repeatedly on the water-bath with sodium amalgam (5 per cent. of sodium). In a short time, the insoluble sodium salt separated, and the quantity was further increased by the addition of more absolute alcohol. The salt, after washing with alcohol in order to remove coumarin, sodium coumarate, and sodium melilotate, was dissolved in water and the solution acidified with hydrochloric acid; on standing for about two days, the acid was deposited in acicular crystals. That this acid is not identical with that obtained by the reduction of hydrodicoumaric acid, is shown by the different solubilities of the sodium salts in alcohol; hydrocoumaric acid is also much more readily soluble in water, and the difference between their calcium salts is most marked.

Calcium Hydrocoumarate, $C_{18}H_{16}O_6Ca + 2H_2O$.

Calcium hydrocoumarate was prepared by boiling a solution of the acid in water with calcium carbonate until no more carbon dioxide was evolved. On filtering off the excess of calcium carbonate and concentrating the filtrate, the salt separated in crystals containing 2 mols. H_2O, which were driven off on heating at 133—140°.

It dissolves only slightly in either hot or cold water; if anything, it is rather more soluble in cold than hot water.

On analysis, the following results were obtained:—

0·1167 gram of the salt, on heating at 140°, gave 0·0101 gram of water, and on addition of sulphuric acid 0·0422 gram of calcium sulphate.

	Calculated for $C_{18}H_{16}O_6Ca + 2H_2O$.	Found.
H_2O	8·00 per cent.	7·97 per cent.
Ca	10·00 „	9·79 „

Hydrocoumarin, $C_{18}H_{14}O_4$.

Hydrocoumaric acid was melted between watch-glasses, and the product after solidifying washed with alcohol till colourless. It was then dissolved in boiling chloroform, and from this solution it separated, on the addition of alcohol, in fine acicular crystals. It melted at 222°, and on analysis gave the following numbers:—

0·2066 gram of the substance gave 0·5596 of CO_2 and 0·09 gram of H_2O.

	Calculated for $C_{18}H_{14}O_4$.	Found.
C	73·47 per cent.	73·87 per cent.
H	4·76 „	4·84 „

The existence of two isomeric acids, having the composition $C_{18}H_{16}O_6$, has thus been proved. Both these acids, when heated, yield an anhydride, $C_{18}H_{14}O_4$, melting at 222—224°. Whether they are identical or not is at present an open question, the identity of the melting points being possibly a mere coincidence. By reconverting the anhydrides into acids and studying the products thus obtained, there is no doubt but that this question could be satisfactorily settled.

If the anhydrides are found to be identical, we have here another case of isomerism similar to that observed by Perkin (*Chem. Soc. J.*, 39, 409) as existing between α- and β-coumaric acids; on the other hand, should they prove to be different, hydrocoumaric acid must have a constitution different from that generally assigned to it.

The investigation of these compounds is being continued. I take the present opportunity of thanking Professor Fittig for the valuable advice he has given me whilst engaged upon the above work.

IX.—*Decomposition of Sodium Carbonate by Fusion.*

By SPENCER UMFREVILLE PICKERING, M.A., Professor of Chemistry at Bedford College.

BERTHELOT ascertained (*Ann. Chim. Phys.*, 29, 311) that anhydrous sodium sulphate after fusion dissolves in water with a considerably greater evolution of heat than it does before fusion; this the author has shown (Trans., 1884, 686) to be due to the existence of the salt in two modifications, the one becoming transformed into the other about 200°. A similar difference of nearly the same extent in the behaviour of fused and unfused sodium carbonate was also observed by Berthelot,* and suggested the idea that this salt, like the sulphate, existed in more than one modification.

In order to investigate the matter, a considerable quantity of the hydrated salt was allowed to effloresce in air, and different portions of it were fully dehydrated at various temperatures; the heat of dissolution of each preparation was then measured. The results are given in the accompanying table (p. 73).† The first eight specimens, dehydrated at temperatures between 60° and the fusing point of the salt, yield identical results, and the fused specimen itself (No. 9) gives a number which is exactly the same as the mean of the others, 5521 cal. No. 1, which was prepared at the lowest temperature, gives a somewhat lower number, 5492 cal., due, probably, to the retention of traces of water, and is therefore omitted from the mean.

As these numbers afforded no explanation of Berthelot's observation, another fused specimen, No. 10, was prepared and examined at three different periods after its preparation. It gave results notably higher (200 cal.) than the other samples, and this excess did not appear to be much diminished on keeping; the result after 48 days (No. 13) is, it is true, somewhat lower than the previous ones, but no great value can be attached to this decrease, as the fused salt dissolves so slowly that the results obtained with it can be regarded as approxi-

---

* Tilden also obtained somewhat discrepant results with different samples (*Proc. Roy. Soc.*, 38, 407).

† For details, see Trans., 1886, 266.

Preparation.	Weight of salt taken.	Water equivalent of the solution, &c.	Initial temp. t.	Rise of temp.	Heat of dissolution		
					at t.	at 18·815° C.	
1. Dehydrated at 60° C.	8·811 grs.	609·83 grams	18·815° C.	0·7498° C.	—	5492 cal.	
2. „ „ 100 „	8·800 „	„	18·815 „	0·7538 „	—	5528 „	5521 cal.
3. „ „ 130 „	8·834 „	„	18·815 „	0·7560 „	—	5524 „	
4. „ „ 155 „	8·821 „	„	18·825 „	0·7556 „	—	5529 „	
5. „ „ 200 „	8·798 „	„	18·815 „	0·7535 „	—	5528 „	
6. „ „ 260 „	8·814 „	„	18·815 „	0·7510 „	—	5500 „	
7. Dehydrated below a red heat	8·792 „	„	18·820 „	0·7503 „	—	5508 „	
8. „ at a red heat	8·719 „	„	18·820 „	0·7404 „	—	5532 „	
9. Fused 24 days previously	8·823 „	„	18·815 „	0·7547 „	—	5521 „	
10. Fused four hours previously	8·817 „	„	18·975 „	0·7811 „	5718 cal.	5710 „	
11. The same after seven days	8·817 „	609·88 grams	21·775 „	0·8020 „	5871 „	5727 „	
[12. Nos. 2—8, mixed	—	—	„	—	5685 „]	—	
13. The same after 41 days more	8·765 „	609·75 „	15·800 „	0·7374 „	5429 „	5646 „	
[14. Nos. 2—8, mixed	—	—	„	—	5304 „]	—	
15. Heated to redness four hours previously	8·784 „	609·88 „	21·775 „	0·7690 „	5651 „	5487 „	
16. Fused and then kept in CO_2 for 20 days	8·781 „	609·71 „	12·855 „	0·6325 „	4646 „	5092 „	
[17. Nos. 2—8, mixed	—	—	„	—	5077 „]	—	
18. Fused 11 days previously	8·813 „	609·66 „	9·95 „	0·6821 „	4995 „	5604 „	
19. The same after being kept in CO_2 for 11 days	8·789 „	„	9·95 „	0·5896 „	4329 „	4938 „	
[20. Nos. 2—8, mixed	—	—	„	—	4912 „]	—	
21. Nos. 2—8, mixed, after being kept in CO_2 for 11 days	8·741 „	609·66 „	9·95 „	0·6630 „	4895 „	5504 „	

mations only. As the dissolutions were not effected at the same temperature, the results obtained with the specimen under examination were compared at each temperature with those given by the normal salt—a mixture of specimens 2 to 8—with which two determinations were made in each case, the mean being given in brackets in the table; this affords the means of reducing all the results to the one temperature of 18·815° C., as has been done in the last column of the table.

Having found a difference in the case of the fused salt, another specimen heated just short of fusion was prepared, No. 15, but it gave the same results as in the previous similar experiment with No. 8. No temperature short of that of fusion will, therefore, induce any change.

It seemed to me possible that fusion had effected a partial decomposition of the carbonate, and in order to test this, a sample which had been fused was kept in a bottle of carbon dioxide for 20 days and then examined (No. 16). Considerable absorption of the gas had taken place, and the salt now gave results more than 400 cal. *below*, instead of above, the normal salt.

This experiment was repeated more fully with Nos. 18 and 19; here the sample which, after keeping 11 days in air, evolved 80 cal. above the normal, when kept for the same time in carbon dioxide, evolved 400 cal. below the normal. In experiment 21, some of the unfused salt which had been kept in carbon dioxide was found to have remained unaltered.

The excess in the heat of dissolution of the fused salt is, therefore, evidently due to a certain amount of the carbonate having been decomposed; and the deficit in the case of the fused salt after exposure to carbon dioxide is not difficult to explain: the carbonate would decompose into oxide, but during the necessary pounding and sifting of the salt this would, no doubt, be converted by atmospheric moisture into the hydroxide, which on exposure to carbon dioxide would give the acid carbonate, a salt which absorbs a considerable amount of heat on dissolution.

The greatest excess noticed (200 cal.) would indicate the conversion of 1·4 per cent. of the carbonate into hydroxide, whilst the greatest deficit noticed would show the presence of about 4 per cent. of the acid carbonate. The hydroxide formed would probably be underestimated owing to its absorbing sufficient water from the air to effect partial hydration, and this excess of moisture would entail the subsequent formation of more of the acid carbonate than would correspond to the hydroxide. The amount of decomposition occurring on simple fusion is probably about 3 per cent.

X.—*The Heat of Hydration of Salts. Cadmium Chloride.*

By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College.

During the recent discussion on the nature of solution at the Birmingham meeting of the British Association, Dr. Nicol drew attention to and laid considerable weight on the supposed fact that the heat of hydration* of cadmium chloride was a negative quantity (*Chem. News*, **54**, 191). His line of argument would appear to be as follows: The heat developed on the hydration of a salt does not give any measure of the affinity of the salt for solid water, for other (unknown) physical changes must occur at the same time, as is proved by the heat of hydration bearing no relation to the degree of hydration, and by the existence of an instance, cadmium chloride, in which the heat of hydration is actually a negative quantity, all spontaneous chemical changes being exothermic. *Quâ* argument this appears to me to be very insufficient. What is observed in the hydration of a salt is repeated in every instance of chemical combination. Thus, in the chlorination of various metals, the heat developed *per* atom of chlorine bears no relation to the number of atoms which are assimilated; and if we are permitted to assume various unknown physical changes as being to a great extent the cause of the heat evolved in the combination of two substances in the same state, we must at once reject all thermochemical evidences. The statement that all spontaneous chemical changes are exothermic is itself robbed of whatever truth it may contain, for we may in every case, as here, doubt the change being a purely chemical one.

My attention had previously been attracted to the case of cadmium chloride, not so much on account of its heat of hydration being negative, but that it was absolutely the only known instance of an inorganic salt where such a fact occurred. As the heat of dissolution of the salts had been determined only once (by Thomsen, *Thermochem.*, **3**, 201), it seemed not altogether improbable that some mistake had arisen, and I therefore determined to repeat the work.

Two samples of the anhydrous salt were prepared, one at 200°, the other being fused. The results which are given in the accompanying table† (see p. 76) can only be regarded as approximations; for, on the one hand, it was found impossible to dehydrate the salt completely without fusion, while, on the other, fusion was impossible without a certain amount of decomposition (the specimen No. 2 contained 0·5 per cent. of oxide). The numbers, however, are sufficiently concordant to show that the fused and unfused salts give practically the same results (3382 and 3211 cal. respectively), and that these are identical with that obtained by Thomsen (3011 cal. at about 18°).

---

* By "heat of hydration," I mean throughout the number obtained after due allowance has been made for the heat of fusion of the water present in the hydrated salt.

† For the calculation of results and other details, see Trans., 1886, 286.

Heat of Dissolution of the Chlorides of Cadmium in 400 H_2O.

Substance.	Weight taken.	Heat equivalent of solution, &c.	Initial temp.	Rise of temp.	Observed heat of dissolution.
$CdCl_2$.					
1 Prep. at 200° C.	15·168 grms.	610·04 grms.	18·14° C.	0·4609° C.	3382 cal.
2. Fused	15·125 „	610·04 „	18·135° „	0·4364 „	3211 „
$CdCl_2,H_2O$.					
3.	16·717 „	611·54 „	18·135 „	0·0853 „	625 „
$CdCl_2,2H_2O$.				Fall of temp.	
4.	18·200 „	613·22 „	18·00 „	0·3104 „	−2284 „

The hydrated salt (No. 3), on dissolution at the same temperature, gave 625 cal., a number evidently identical with that obtained by Thomsen—760—but on analysis it was found to consist of a monohydrate, instead of a dihydrate as Thomsen states, containing 9·617 per cent. water; theory, 9·120 per cent.

This monohydrate was uniformly obtained whenever a solution of the salt was evaporated at a high temperature; when, however, a cold solution was evaporated, crystals, not easily distinguishable from the monohydrate, were obtained, but consisting of the dihydrate, containing 17·035 per cent. water, the theoretical number being 16·450 per cent. This dihydrate, on dissolution, absorbed 2284 cal.

It is evident, therefore, that some error must have occurred in Thomsen's statement; he certainly used the monohydrate in the calorimetric determination, and, unless his entry that it was found on analysis to contain 2·01 H_2O be a mere *lapsus calami*, it is probable that the analysis was performed on a different specimen, prepared, as he imagined, under identical conditions, but in reality at a lower temperature.

According to the numbers here given, the heat of hydration of cadmium chloride is by no means a negative quantity [$CdCl_2 + H_2O$

(solid)* being 1092 cal., and [$CdCl_2 + 2H_2O$ (solid)] 2421 cal. or 1210 × 2, numbers which are considerably larger than in the case of sodium carbonate (588 cal. per H_2O), strontium nitrate (421 cal.), and sodium sulphate (320 cal.).

Amongst organic substances, there is one salt in which the heat of hydration would appear to be negative, sodium benzenesulphonate, − 250 cal. per H_2O, besides the case of racemic acid, in which it is exactly *nil*. This latter instance has been well established, and, in my opinion, tends to show that the so-called hydrated acid does not contain water of crystallisation at all, but possesses a constitution different from that of the anhydrous acid; a similar explanation may hold good with the sodium benzenesulphonate, but, as this instance rests at present on one determination only (Berthelot's), it should in the first place be more fully investigated.

XI.—*Contributions from the Laboratory of Gonville and Caius College, Cambridge.* No. VIII. *On Bismuthates.*

By M. M. PATTISON MUIR, M.A., Fellow, and DOUGLAS J. CARNEGIE, B.A., Scholar, of Gonville and Caius College.

DOES hydrated bismuthic oxide, Bi_2O_5,H_2O, exhibit acidic functions in its reactions with alkalis?

1. Experiments described in former papers by one of us (see especially *Chem. Soc. J.*, 1876, i, 144; 1877, i, 24; and ii, 131; 1878, 197) failed to demonstrate the existence of any definite bismuthate of potassium, but at the same time they showed that unstable combinations of Bi_2O_5 (or Bi_2O_4) with K_2O probably exist in presence of much potash, and that these combinations, assuming them to exist, are decomposed when the excess of potash is removed by washing with water.

2. Since these experiments were published C. Hoffmann has contributed to the *Annalen* a paper on bismuthates (*Annalen*, **223**, 110). He suspended BiO_3H_3 in concentrated cold potash solution, saturated the liquid with chlorine, added more potash, boiled, again saturated with chlorine, added potash, boiled, and repeated this treatment until apparently homogeneous reddish-brown solids were obtained; he washed these solids, usually first with cold, and then with boiling water, until the washings ceased to show an alkaline reaction; he then

---

* The latent heat of fusion of H_2O at 18° being 1580 cal.

dried the solids over sulphuric acid, and analysed them. Hoffmann also chlorinated Bi_2O_3 suspended in concentrated potash solution, and treated the violet-brown solid produced as already described. He found that every one of his preparations contained bismuth, oxygen, and potassium, and that the masses of the first and second were present in the ratio $Bi_2 : O_x$, where $x > 3$. Hoffmann deduced formulæ for the compounds he had prepared on the supposition that they were bismuthates, hypobismuthates, or compounds of these salts with oxides of bismuth; his chief results are presented in the following table :—

Bismuth compound used.	Sp. gr. of KOH,Aq used.*	Product obtained.	Remarks.
BiO_3H_3.	1·08	$2KBiO_3,4Bi_2O_5,Bi_2O_3$	
"	"	$2KBiO_3,5Bi_2O_5$	Chlorinated three times.
"	1·128	$2KBiO_3,5Bi_2O_5$	
"	1·539 (but *v. infra*)	$KBiO_3,Bi_2O_5$	
Bi_2O_3	"	$4KBiO_3,6Bi_2O_5,Bi_2O_3$	
"	"	$KBiO_3,Bi_2O_3$	Washed with cold water.
BiO_3H_3	"	KBi_2O_4	BiO_3H_3, suspended in hot KOH,Aq ; product washed with water at 50—60°.

We think that the formulæ given by Hoffmann as expressing the composition of so-called bismuthates are of very little value.

(1.) His methods of analysis were unsatisfactory; he determined bismuth by precipitation as BiOCl from solutions in hydrochloric acid, by adding water; but the whole of the bismuth in a solution in hydrochloric acid is not precipitated when addition of water ceases to produce any visible formation of BiOCl: he determined potassium in the filtrate from the oxychloride of bismuth by evaporating to dryness, converting the potassium chloride into sulphate, and weighing; but our experiments (*vide* Appendix) prove that the substance weighed as potassium sulphate must have contained considerable traces of silica, besides oxides of (iron) aluminium, and calcium.

(2.) He seems, generally, to have made one preparation of each compound, and to have determined the bismuth and potassium in this; but our experiments show that it is almost impossible to obtain substances of the same composition in successive experiments, although the experimental conditions are kept as nearly as may be the same.

---

* The symbol Aq is used after the formula of a compound to signify an aqueous solution of that compound.

(3.) He asserts that the compounds analysed by him did not contain water; in every case in which we made direct determinations we found that water was obtainable from the substances prepared by us under conditions very similar to, if not identical with, those employed by Hoffmann.

Incidentally we may remark that Hoffmann says that the most concentrated solution of potash he used was prepared by dissolving 1 part KOH in 2 parts of water, and that it had the sp. gr. 1·539; by repeated experiments we found that the solution of potash thus prepared has the sp. gr. (about) 1·28, and that to obtain a solution sp. gr. 1·539 about 2 parts KOH must be used for 1 part of water.

3. We suspended 1 part (1) BiO_3H_3 (2) BiOCl in about 10 parts of cold aqueous potash, sp. gr. (*a*) 1·539, (*b*) 1·13, (*c*) 1·08, passed chlorine into the liquids until the smell of chlorine was apparent, added as much potash solution as was originally used, boiled till the smell of chlorine was removed, again chlorinated, added more potash solution, boiled, and repeated this treatment until apparently homogeneous solids were produced (see Hoffmann, *loc. cit.*).

4. Here we may remark that it is extremely difficult to obtain BiO_3H_3 free from oxychloride or oxynitrate. When a solution of bismuth oxide or carbonate in hydrochloric acid reacts with aqueous potash a precipitate of hydrated bismuthous oxide mixed with bismuth oxychloride is obtained; the oxysalt cannot be removed by washing with cold water; long-continued treatment with hot water changes part of the oxychloride to oxide and hydrochloric acid, but at the same time part of the hydrated oxide is dehydrated. The best method we have tried for preparing BiO_3H_3 approximately pure is to dissolve the metal or the nitrate in as small a quantity of nitric acid as possible, to pour the solution into an excess of concentrated ammonia solution, to wash the precipitate repeatedly by decantation with cold water, then to shake the precipitate for long periods with extremely dilute sodium carbonate solution, and finally to remove the carbonate by washing with cold water. By this method, we obtained BiO_3H_3 free from oxynitrate, but containing small traces of carbonate or oxycarbonate of bismuth.

5. We shall first consider the results obtained when potash solution of sp. gr. 1·539 was used. Oxidation from the form Bi_2O_3 to Bi_2O_4 and Bi_2O_5 proceeds rather more rapidly when BiOCl than when BiO_3H_3 is used. In either case the final product is a dark reddish-brown, heavy, apparently homogeneous, solid. The solids thus obtained were washed by decantation with cold water; after a few washings they ceased to settle quickly; after a few more washings separation of the solids into two parts became apparent; one part was always dark-red, and settled fairly well; the other part was

always yellow-red, and settled very slowly. By repeated and systematic washing in a series of vessels we attempted to separate the two parts; the lighter solid settled better in shallow flat dishes. By standing in contact with very dilute potash for some weeks in a stoppered bottle this lighter body became darker, and could then be filtered. The washing of each solid was continued until the washings did not affect the colour of small scraps of red litmus-paper when the paper had remained in the liquid for 24 hours. In a few cases, in which the treatment of BiO_3H_3 with chlorine and potash, as described, was repeated five or six times, we found that the solid finally obtained settled fairly well when washed with cold water, and that comparatively little of the lighter, slowly settling, compound was produced. In some cases, after separating the lighter solid we suspended it in potash solution, sp. gr. 1·539, and repeated the treatment with chlorine, but in no case did we succeed in changing much of it to the heavier and darker coloured compound. The solids were dried at 100° and analysed (for methods of analysis see Appendix).

A. Heavy, dark-red solids; obtained by chlorinating in potash solution, sp. gr. 1 539; washed with cold water, dried at 100°. Analyses made with products obtained at different times, working with different quantities of materials.

		Analyses of products; percentages.		
Compound used.		Bi.	K.	H_2O.
BiOCl	(1)	76 94	4·62	2·57
BiOCl	(2)	75·33	3·5	2·0
BiOCl	(3)	74·34	1·5	—
BiO_3H_3	(1)	82·75	4·94	—
BiO_3H_3	(2)	76·2	5·3	—
BiO_3H_3	(3)	77·29	3·69	—

B. Lighter, yellow-red solids; obtained by chlorinating in potash sp. gr. 1·539; washed with cold water, dried at 100°. Analyses made with products obtained at different times, working with different quantities of materials.

		Analyses of products; percentages	
Compound used.		Bi.	K.
BiOCl	(1)	78·25	4 07
BiOCl	(2)	74·24	8·64
BiOCl	(3)	70 56	—
BiOCl	(4)	73·41	—
BiO_3H_3	(1)	77·25	9 29

The quantities of potassium are very doubtful; the potassium sulphate invariably contained traces of silica, alumina, lime, and magnesia, and generally also ferric oxide (see Appendix).

6. The darker and heavier solids, from which all potash removable by cold water had been removed, were now washed with boiling water; in some cases they were subjected to the continuous action of boiling water for some hours. In every case, the washings were distinctly alkaline; washing was continued until the washings had no effect on the colour of scraps of red litmus-paper after being in contact with them for 24 hours; very long-continued washing was necessary to produce this result. This process always brought about the formation of much yellow-red solid which settled extremely slowly; in most of those cases in which the action of boiling water was continuously maintained for some hours, the whole of the heavier and darker solids were changed to the lighter substances; in other cases, we obtained some grams of heavy, dark-red solids from which all potash removable by the action of water at about 97—98° had been removed. These dark, heavy solids were dried at 100°, and analysed; the lighter, yellow, solids, produced as described, were also washed with hot water, dried at 100°, and analysed.

C. Heavy, dark-red solids; obtained by washing compounds, analyses of which are given under A, with nearly boiling water, and drying at 100°.

		Analyses, percentages.			O above that requred to form Bi_2O_3*
Compound used.		Bi.	K.	H_2O.	(see Appendix).
BiOCl......	(1)	83·61	4·06	—	—
BiO_3H_3	(1)	75·6	traces (not more than 0·5)		
BiO_3H_3	(2)	72·6	1·48	5·2	5·9
BiO_3H_3	(3)	85·06	0·70	—	—

D. Lighter, yellow solids; obtained under the same conditions and from the same sources as those analysed under C; washed with hot water, dried at 100°.

		Analyses, percentages.			O above that required to form Bi_2O_3
Compound used.		Bi.	K.	H_2O.	(see Appendix).
BiOCl......	(1)	75·2	5·66	—	—
BiOCl......	(2)	73·8	6·89	—	—
BiO_3H_3	(1)	78·89	1·61	—	—
BiO_3H_3	(2)	79·4	—	2·82	3·9

---

* By oxygen above that required to form Bi_2O_3 is meant the oxygen obtained by heating the substances in a vacuum in connection with a Sprengel pump.

7. The solid products of the long-continued reaction between either BiO_3H_3 or BiOCl, concentrated potash, and chlorine, are evidently non-homogeneous, whether they are washed with cold or with hot water until all potash removable by such washing is removed. We have found, however, that if chlorination is continued for a sufficient time, the product well washed with cold, and then with boiling water, is then dried at 100°, and again washed with boiling water, and this process of drying at 100° and washing with boiling water is repeated until the washings are without the slightest action on red litmus-paper after at least 24 hours' contact, a homogeneous product is obtained, free from potassium, and composed of bismuth, oxygen, and water, in the ratio $Bi_2 : O_5 : H_2O$.

The best method, however, for preparing Bi_2O_5,H_2O is that recommended in a former paper by one of us, viz., to chlorinate BiO_3H_3, or Bi_2O_3, suspended in hot potash solution, sp. gr. about 1·35, to wash the product a few times with hot water, then to treat with a very little concentrated nitric acid, to wash with dilute nitric acid and finally with water, and to dry at 100°.

8. Although the products obtained as described vary in composition, yet it appears that those which have been fully analysed usually contain bismuth and oxygen nearly in the ratio $Bi_2 : O_5$. Thus, take analysis (1) from BiOCl, under the heading A (par. 5); let it be assumed that the compound contains K_2O; calculate the K to K_2O, add this to the Bi and H_2O, and deduct the sum from 100; the difference represents O combined with Bi; the ratio of $O : Bi = 1 : 5·16$; the ratio of O to Bi in $Bi_2O_5 = 1 : 5·23$. This treatment of the analytical data assumes that the compounds in question contain K_2O; one direct argument in favour of this is the fact that when washing with water was nearly finished, a piece of red litmus-paper immersed in the water above the solid matter showed no change of colour for hours, but when the paper was moved downwards, so that part of it came into contact with the suspended solid, the colour of the litmus was slowly but appreciably changed.

9. The composition of the products obtained by passing chlorine into potash solution of sp gr. 1·13 and 1·08, respectively, holding (1) BiO_3H_3, and (2) BiOCl, in suspension, was found to be as follows (p. 83).

None of these products could be regarded as homogeneous; they all contain potassium, probably as K_2O, and water; the analyses prove little beyond the non-homogeneity of the products of the action of chlorine under the conditions described.

10. But the extreme slowness with which potash is removed from the substances we have described, the fact that when cold water has ceased to affect them hot water still dissolves out potash, and the

E. Solids obtained by chlorinating in potash solution sp. gr. 1·13.

Compound used.	Analyses of products; percentages.		Method of washing.	Remarks.
	Bi.	K.		
BiOCl......	70·6	9·5	With cold water	Very dark puce colour; settled fairly well.
BiO_3H_3	83·2	2·3		
BiO_3H_3	74·3	1·9	With boiling water	Dark, heavy, puce colour: settled well; washed for 10—15 days.
BiO_3H_3	74·2	6·0	With cold water	Light-brown; settled slowly.
BiO_3H_3	74·5	4·6	With cold water	Very light yellow-brown; settled very slowly; washing continued for several weeks.

F. Solids obtained by chlorinating in potash solution sp. gr. 1·08.

BiOCl......	84·8	1·0	With cold water	Very dark brown, heavy; settled fairly well.
BiOCl......	—	*2·8	With boiling water	Dark brown; settled fairly well.

changes in their appearances when they are shaken with water, suggest that during the chlorination of BiO_3H_3 and BiOCl suspended in very concentrated potash solution, compounds may be produced of the form $x Bi_2O_5$(or $x Bi_2O_4$),$y K_2O$, in which Bi_2O_5 (or Bi_2O_4) acts as the more negative part, and K_2O as the more positive part of each compound. We have not been able to isolate such compounds; but we regard the experiments to be described as pointing to the existence of compounds of the form indicated in presence of very large quantities of potash.

11. Moist bismuthic hydrate (Bi_2O_5,xH_2O) containing a little potash was added in very small successive quantities to boiling potash solution so concentrated that solidification began immediately after removing the source of heat; the Bi_2O_5,xH_2O dissolved without changing the colour of the potash. We found that one part KOH would dissolve (roughly) about $\frac{1}{100}$th part Bi_2O_5,H_2O. The whole

Analysis made on a very small quantity.

solidified on cooling; enough water was then added to form a clear solution, but from this solution, exposed to air, yellowish-white or reddish-white solid matter began to separate. In some cases, we nearly neutralised the solution with hydrochloric acid; in other cases we allowed the solution to remain in the air until precipitation ceased; in every case the whole of the bismuth held in solution by the potash was found in the precipitated solids. The solid products, varying in appearance from nearly white to reddish-white, were washed (by decantation) with cold, and then with boiling water, until the washings ceased to affect the colour of red litmus-paper after 24 hours' contact; washing was usually continued for 10—15 days before this result was obtained; the substance was then dried at 100°. If so much Bi_2O_5,xH_2O was added to the boiling potash that a little remained undissolved, the precipitation of yellow or red-yellow solid began as soon as water was added to the solid mass after cooling; in these cases we added more water, filtered quickly through glass-wool, and proceeded with the filtrates as already described. The results of our analyses are presented in the table G, p. 85.

The analyses of (2) and (4) (see table) fairly agree with the numbers required for Bi_2O_4, viz, Bi = 86 66, O above Bi_2O_3 = 3·33. The analysis of (3) seems to point to this substance being nearly pure Bi_2O_3 (Bi_2O_3 requires Bi = 89·65 per cent.). These substances are evidently not quite homogeneous; but we regard the results of the analyses, especially (2) and (4), as distinctly in favour of the supposition that when Bi_2O_5,xH_2O dissolves in much potash containing a little water, it reacts chemically with a portion of the potash, and that the compound or compounds formed are slowly decomposed by water with production of potash solution and Bi_2O_3 containing more or less Bi_2O_4 or even Bi_2O_5.

12. These results suggest the probability that during the reaction between BiO_3H_3 or BiOCl, very concentrated potash solution, and chlorine, some of the Bi_2O_5,xH_2O produced dissolves in the potash. We therefore chlorinated a quantity of BiO_3H_3 in potash solution, sp. gr. 1·539, in the manner already described, and nearly neutralised (by hydrochloric acid) the potash solution decanted from the reddish solid matter; a white, bulky, precipitate was produced; this was washed with cold, and then with hot water, until the washings did not affect the colour of red litmus-paper after 24 hours' contact, dried at 100°, and analysed. The product contained about 6 per cent. of potassium, about 15 per cent. water, and very distinct traces of the oxides of aluminum, silicon, calcium and magnesium; no oxygen was given off when it was heated to bright redness in a vacuum in connection with a Sprengel pump. We did not think it necessary to estimate bismuth; the substance evidently consisted of BiO_3H_3 (re-

quires 10·5 per cent. H_2O) containing potash, and various impurities derived from the porcelain vessels used in its preparation.

13. Attempts were made to isolate definite compounds of Bi_2O_5 (or Bi_2O_4) with K_2O, by dissolving Bi_2O_5,xH_2O in boiling potash with a very little water, as already described, allowing to cool, adding just enough water to effect solution, evaporating in a vacuum over sulphuric acid, collecting the yellow solid which separated, and washing with absolute alcohol. The results, however, were similar to those described in paragraph 11; no definite compound could be obtained.

G. Solids obtained by dissolving Bi_2O_5,xH_2O in much potash with a little water, dissolving in water, nearly neutralising by hydrochloric acid, or by the carbon dioxide, &c., of the air, washing with boiling water, and drying at 100°.

I. *Bi_2O_5,xH_2O prepared from BiOCl.*

Method of preparation and remarks.	Analyses; percentages.			O above that required to form Bi_2O_3* (see Appendix).
	Bi.	K.	H_2O.	
(1.) All Bi_2O_5,xH_2O used dissolved in potash; precipitation effected by adding water and allowing to stand in air. Lustrous, yellowish-white, crystalline, solid	(1) 85·4	Trace; not more than 0·3	—	—
	(2) 84·2	—	—	—
(2.) A little Bi_2O_5 remained undissolved in potash; water added, liquid at once filtered through glass-wool, and nearly neutralised by hydrochloric acid. Yellowish-white, lustrous, solid	87·5	decided traces	0·78	2·75

II. *Bi_2O_5,xH_2O prepared from BiO_3H_3.*

Method of preparation and remarks.	Bi.	K.	H_2O.	O above that required to form Bi_2O_3* (see Appendix).
(3.) All Bi_2O_5,xH_2O dissolved in potash, &c., as under I (1). Yellow-white, lustrous, solid	90·0	none	—	—
(4.) A little Bi_2O_5 remained undissolved in potash, &c., as under I (2). Reddish-white, lustrous, solid	85·45	none	1·52	3·35

---

* See foot note on p. 81.

14. From the experiments described in the foregoing paragraphs, we conclude—

I. That the solid obtained as the final product of the reaction between BiO_3H_3, or BiOCl, large excess of very concentrated potash solution, and chlorine, after very long-continued washing with nearly boiling water, has the composition Bi_2O_5,H_2O.

II. That Bi_2O_5,H_2O exhibits feebly acidic functions in its reactions with a large mass of very concentrated potash solution.

III. That it is very difficult, probably it is impossible, to isolate compounds of the form $x Bi_2O_5,y K_2O$, or $x Bi_2O_4,y K_2O$, but that such compounds probably exist in presence of much potash and little water.

IV. That the formulæ assigned by Hoffmann (*Annalen*, **223**, 110) to so-called bismuthates of potassium are of little if any value.

APPENDIX.

Methods of Analysis.

Bismuth was usually determined by the ordinary method of precipitating with ammonium carbonate from a slightly acid (nitric acid) solution, &c.; experiments made to test the accuracy of this method showed that the experimental error was about 0·4 per cent. Bismuth was sometimes determined by dissolving in as small a quantity as possible of hydrochloric acid, nearly neutralising by ammonia, precipitating by a large quantity of water, allowing to stand in a warm place for 12 hours, collecting the bismuth oxychloride on a weighed filter, washing, drying at 110°, and weighing. Experiment showed that the experimental error was about 0·3 per cent. A trace of bismuth invariably remained unprecipitated as oxychloride; attempts were made to precipitate and weigh this as sulphide, but the results were always a few per cent. too high; it is known that moist bismuthous sulphide easily oxidises while being dried in air. Too much stress must not be put on these experiments; they suffice to show that the differences between the determinations of bismuth are not to be set down to experimental errors in the methods of estimation employed.

Potassium was determined (1) by dissolving in a very little hydrochloric acid, precipitating bismuth oxychloride by addition of much water, filtering after 12 hours, precipitating traces of bismuth remaining in solution by sulphuretted hydrogen, filtering, removing sulphuretted hydrogen by boiling, precipitating traces of iron and aluminium oxides by addition of ammonia, and lime by ammonium oxalate, evaporating to dryness at 100°, heating until all ammonium salts were removed, dissolving in water, filtering, adding platinum chloride, and proceeding by the ordinary method for estimating potassium as platinochloride; (2) by dissolving in nitric acid, precipitating by ammonia and ammonium carbonate, filtering, removing iron oxide, &c., as in (1), evaporating to dryness, heating to remove ammonium nitrate, and determining potassium, sometimes as platinochloride, sometimes as sulphate. We found method (1) better than (2); it is much easier to remove ammonium chloride than ammonium nitrate by heating, the latter salt is very liable to spirt when strongly heated. The platinic chloride used was afterwards found to contain some impurities which would tend to increase the apparent percentage of potassium. When traces of potassium are noted as present, the observation is based on experiments made after removing bismuth, &c., as described, and examining, in some cases by the ordinary flame test, in other cases, where this test gave no positive result, by the spectroscope.

Water was estimated by heating in a current of dry air, and collecting the water in a weighed calcium chloride tube, a blank experiment being made with the apparatus used. Sometimes water was determined at the same time as the oxygen above that required to form Bi_2O_3; in these cases, the substance was heated in a piece of hard glass tubing connected with a weighed chloride of calcium tube, which was again connected with a Sprengel pump. The gas evolved was always shown to be absorbed by alkaline pyrogallate.

XII.—*Derivatives of Tolylbenzene.*

By Thomas Carnelley, D.Sc. (Lond.), and Andrew Thomson,
M.A., D.Sc. (Edin.), University College, Dundee.

In a former paper (this Journal, Trans., 1885, 47—586) we described one monobromotolylbenzene and two dibromophenylbenzoic acids, but were unable to separate the dibromotolylbenzenes from which these latter were derived. The present paper gives an account of the preparation of another monobromotolylbenzene, the separation of the dibromo-compounds, and the formation of new oxidation-products from these.

I. *Monobromo*-1,4-*Tolylbenzene.*

a-Bromotolylbenzene, $C_6H_5 \cdot C_6H_3Br \cdot CH_3 = [1:2 \text{ or } 3:4]$.—To prepare this compound, 15·5 grams of toylbenzene were dissolved in carbon bisulphide, and 14·8 grams of bromine slowly added to the mixture. After the chemical action had ceased, the flask containing the mixture was gradually heated for two hours with a reflux condenser. The carbon bisulphide was next distilled off, the residue in the flask treated with excess of caustic soda to remove the hydrobromic acid, then well washed with water, and finally extracted with boiling alcohol. From this, a mass of crystals, A, separated on cooling, and on evaporating the mother-liquor a yellowish oil, B, was obtained. When purified by further crystallisation, the portion A melted at 127—129°, and in other respects exhibited properties exactly similar to those of the monobromotolylbenzene previously described. On oxidation with either excess or deficit of chromic and glacial acetic acid, it gave monobromoterephthalic acid (m. p. 304—306° corr.), as proved by its general properties and by analysis. No intermediate product of oxidation could be obtained. The formation of monobromoterephthalic acid as a final product of oxidation proves that the monobromotolylbenzene must have the constitution $C_6H_5{\cdot}C_6H_3BrMe$ = [1 : 2 or 3 : 4]. The monobromoterephthalic acid obtained as above described sublimed very easily on heating in an open tube, yielding a sublimate which melts at 243—245°. This is probably the anhydride, though the quantity of material at our disposal was not sufficient for an analysis.

β-Bromotolylbenzene, $C_6H_4Br{\cdot}C_6H_4Me$ = [1′ : 4′ : 1 : 4].—The yellow oil B was freed from alcohol and moisture first by heating it for some time to nearly 100°, and afterwards by exposing it for about three weeks over strong sulphuric acid. When cooled to a low temperature, the oil solidified to a yellow crystalline mass, which melted at 27—30°, and on analysis gave the following results :—

	Calculated.	Found.
$C_{13}H_{11}Br$	32·38	32·03 per cent. Br.

This compound is therefore an isomeride of the crystalline monobromotolylbenzene previously described, and differs from it chiefly in having a much lower melting point, and in being more soluble in alcohol. On oxidation with a deficit of chromic and glacial acetic acids, a product was obtained which was only partly soluble in ammonia. The soluble part after purification melted at 193—194°, and was easily soluble in cold ether, though but sparingly soluble in alcohol and benzene. It gave the following result on analysis, proving it to be a monobromophenylbenzoic acid :—

	Calculated.	Found.
$C_{13}H_9BrO_2$	28·88	28·38 per cent. Br.

On treating another portion of the oil with a large excess of the same oxidising agents, a pure white compound was obtained, readily soluble in ammonia and melting at 247—249°. The residue, insoluble in ammonia in the former oxidation, was also treated with excess of oxidising agents, when the product was found to be easily soluble in ammonia, and melting at 248—249°. On analysis, both these products gave the same result, which, with the melting point, proves the compound to be 1,4 bromobenzoic acid, $C_6H_4Br{\cdot}COOH$. The monobromotolylbenzene, melting at 27—30°, therefore on oxidation gives first a monobromophenylbenzoic acid, $C_6H_4Br{\cdot}C_6H_4{\cdot}COOH = [1' : 4' : 1 : 4]$, and finally monobromobenzoic acid, $[C_6H_4Br{\cdot}COOH = 1 : 4]$.

II. *Dibromotolylbenzenes*, $C_{13}H_{10}Br_2$.

α-Dibromotolylbenzene, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}CH_3 = [1' : 4' : 1 : 2 \text{ or } 3 : 4]$ — 35·6 grams of bromine were slowly added to 18·7 grams of tolylbenzene dissolved in carbon bisulphide, and the chemical action moderated by keeping the flask in cold water. After allowing the contents to remain together for about 12 hours, the flask was gently heated with a reflux condenser for two hours, and the carbon bisulphide distilled off. The residue was well washed with caustic soda, and afterwards with water, and was then repeatedly boiled for a considerable time with excess of alcohol, in which only a small part A was soluble, the bulk of it remaining as an insoluble mass B. The part A, after several crystallisations from hot alcohol, was obtained in exceedingly beautiful, transparent, ferny plates, melting at 113—115°, giving on analysis results agreeing with a dibromotolylbenzene:—

	Calculated.	Found.
$C_{13}H_{10}Br_2$	49·02	48·52 per cent. Br.

A portion of this on partial oxidation gave an acid melting at 202—204°, moderately soluble in alcohol, and easily soluble in ether and benzene. Its properties, melting point, and analysis agree with those of the dibromophenylbenzoic acid described in our last paper. On oxidation with a large excess of chromic and glacial acetic acids, an acid was obtained melting at 248—249°, and corresponding in all other respects with 1,4 bromobenzoic acid. These facts prove that one of the bromine-atoms is in the benzene-group, and one in the tolyl group, and that the one in the benzene-group must be in the para-position; α-dibromotolylbenzene on oxidation therefore gives first dibromophenylbenzoic acid, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}COOH = [1' : 4' : 1 : 2 \text{ or } 3 : 4]$, and finally bromobenzoic acid, $C_6H_4Br{\cdot}COOH = [1 : 4]$, and has consequently the constitution ascribed to it above.

β-Dibromotolylbenzene, $C_6H_4Br{\cdot}C_6H_3Br{\cdot}CH_3 = [1' : 4' : 1 : 3 \text{ or } 2 : 4]$. —The mass B, which was almost insoluble even in hot alcohol, was so easily soluble in benzene that definite crystals could not be obtained.

Treatment with ether, however, yielded needle-shaped crystals, which, after purification, melted at 148—150°, and gave on analysis the following results :—

	Calculated.	Found.
$C_{13}H_{10}Br_2$	49·02	48·67 per cent. Br.

On partial oxidation, it gave an acid which melted at 231—232°, and contained the following percentage of bromine :—

	Calculated.	Found.
$C_{12}H_7Br_2\cdot COOH$....	44·94	44·77 per cent. Br.

This acid corresponds with the one described in our previous paper, and like it sublimes easily and almost completely without melting, and is therefore *β-dibromotolylbenzoic acid*,

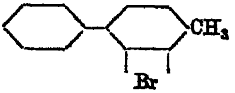
$$C_6H_4Br\cdot C_6H_3Br\cdot COOH = [1' : 4' ; 1 : 3 \text{ or } 2 : 4].$$

Oxidation with a large excess of chromic and glacial acetic acids gives an acid melting at 250—251°, and in all other respects similar to parabromobenzoic acid. A residue, insoluble in ammonia, left in the previous partial oxidation, also gave parabromobenzoic acid, melting at 249—251°, when treated with excess of the oxidising agents. β-Dibromotolylbenzene, on oxidation, therefore gives first dibromophenylbenzoic acid, $C_6H_4Br\cdot C_6H_3Br\cdot COOH = [1' : 4' : 1 : 3$ or $2 : 4]$, and finally bromobenzoic acid, $[C_6H_4Br\cdot COOH = 1 : 4]$, and hence has the constitution ascribed above.

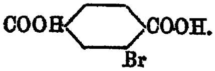
It thus appears that the difference in the properties and melting points of the α- and β-dibromotolylbenzenes arises from the fact that in the one the bromine in the tolyl-ring is in the ortho-position, and in the other in the meta-position, but which of these two positions is to be ascribed to the two compounds respectively we have as yet had no means of deciding.

The results above described may be expressed in the following tabular scheme :—

I. *Mono-bromo-Compounds.*

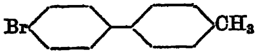


α-Bromotolylbenzene.
M. p. = 129°.

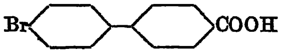


Bromoterephthalic acid.
M. p. = 304—306°.

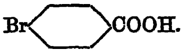
No intermediate oxidation-product could be obtained.



β-Bromotolylbenzene.
M. p. = 27—30°.

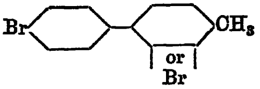


Bromophenylbenzoic acid.
M. p. = 193—194°.

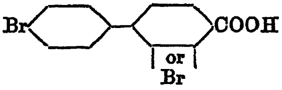


Bromobenzoic acid. M. p. = 247—249°.

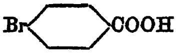
II. *Dibromo-Compounds.*



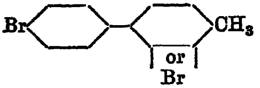
α-Dibromotolylbenzene.
M. p. = 113—115°.



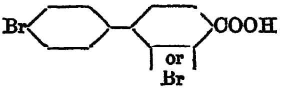
α-Bromophenylbromobenzoic acid.
M. p. 202—204°.



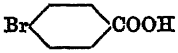
Bromobenzoic Acid. M. p. = 249—251°.



β-Dibromotolylbenzene.
M. p. = 148—150°.



β-Bromophenylbrombenzoic acid.
M. p. = 231—232°.



Bromobenzoic acid. M. p. 249—251°.

The two dibromophenylbenzoic acids referred to above and melting at 202—204° and 231—232° respectively, are isomeric with the dibromophenylbenzoic acid described by Holm (*Ber.*, **16**, 1082; and Abstr., **44**, 922), and which he obtained by fusing β-dibromofluorene ketone with caustic potash. Holm's acid is consequently a derivative of 1,2 phenylbenzoic acid, whereas both our acids are derived from 1,4 phenylbenzoic acid.

XIII.—*The Amount of Chlorine in Rain-Water collected at Cirencester.*

By Edward Kinch, Royal Agricultural College, Cirencester.

The determinations of chlorine in rain-water which follow were commenced by Professor A. H. Church in 1870, and have been continued without intermission since, up to 1879 by Church, till 1881 by Dr. E. W. Prévost, and since then by myself. All the rain-water collected in the rain-gauge of the College, which is a third-class Meteorological Station, is preserved for analysis. Until 1879, the gauge was in the botanic garden, 434 feet above the mean sea-level, it was then moved to the kitchen garden, to a position 443 feet above sea-level, where it still remains. The gauge is 5 inches in diameter and 1 foot above the surface of the ground. The water falling during the six winter months, October to March inclusive, is kept separate from that falling during the six summer months, April to September inclusive; the chlorine is determined in the mixed waters of each six months.

During the first years, the chlorine was determined volumetrically in the water directly without evaporation; probably the results thus obtained are slightly too high. Now, the determinations are made volumetrically after evaporating the sample down to about one-fifth of its original bulk, some pure lime-water being added to the liquid before commencing the evaporation. The amount of chlorine is estimated by using a standard silver nitrate solution with potassium chromate as an indicator.

The six months ending March 31st, 1873, show a most exceptionally high amount of chlorine, namely, 17·92 parts per million of water; of this period, the first three months, October, November, and December, 1872, were characterised by boisterous winds, mostly from the S.W., and by almost continuous wet. The presence of an abnormal amount of chlorine in the rain at Cirencester can almost always be traced to salt spray from the Bristol Channel, which is about 35 miles distant. On different occasions, immediately after a storm from the S.W., crystals of common salt have been found on the windows of the college facing west. In some rain-water collected during a storm on September 13th, 1869, Professor Church found 58·17 parts of chlorine per million, equivalent to 6·71 grains of common salt per gallon. In the six months ending March 31st, 1880, there was also a large amount of chlorine in the rain, but the rainfall had then been very much below the average, and the total amount of chlorides deposited was but slightly above the average.

At Rothamsted, during the same time, especially in November, 1879, the amount of chlorine in the rain-water was very high. The possibility that the sample of rain-water for the period ending March,

Period, six months ending—		Rainfall in inches.	Chlorine per million.	Equivalent to NaCl grains per gallon.	Equivalent to NaCl lbs. per acre.
1870.	Sept. 30	9·05	2·63	0·303	8·86
1871.	March 31............	12·76	2·82	0·325	13·40
„	Sept. 30	21·06	2·39	0·276	18·77
1872.	March 31............	15·01	2 14	0·247	11·98
„	Sept. 30	17·15	4·72	0 545	30·12
1873.	March 31...........	20·45	17·92	2·067	136·61
„	Sept. 30	12·81	2 72	0 314	13·00
1874.	March 31............	11·97	1·64	0·189	7·31
„	Sept. 30	13·21	4·18	0·482	20·58
1875.	March 31............	17·83	3·90	0·450	25·93
„	Sept. 30	17·26	2·49	0·287	16·01
1876.	March 31............	24·51	2·31	0·266	21·07
„	Sept. 30	14·07	4·47	0·516	24·46
1877.	March 31............	22·78	3·19	0·368	27·09
„	Sept. 30	19·27	4·97	0·573	35·68
1878.	March 31............	15·03	4·73	0·546	26·52
„	Sept. 30	17·41	2·55	0·294	16·54
1879.	March 31............	19·58	2·37	0·273	17·27
„	Sept. 30	26·20	3·46	0·399	33·78
1880.	March 31............	8·51	10·38	1·197	32·92
„	Sept. 30	18·44	2·34	0·270	16·09
1881.	March 31............	19·53	3·41	0·394	24·87
„	Sept. 30	15·12	2·43	0·280	13·68
1882.	March 31............	15·45	3·02	0·348	17·37
„	Sept 30	22·34	2·22	0·256	18·48
1883.	March 31............	22·89	2·60	0·300	22·19
„	Sept. 30	14·72	2·23	0·257	12·23
1884.	March 31............	14·73	4·78	0·551	26·23
„	Sept 30	12 59	3·53	0·407	16·56
1885.	March 31............	13·78	4·83	0·557	24·86
„	Sept. 30	13·26	3·01	0·347	14·87
1886.	March 31............	17·23	2·56	0·295	16·43
„	Sept. 30	14·72	1·79	0·207	9·85
Mean of 16 summer periods: 1870 to 1885		16·54	3·14	0·363	19·36
Mean of 16 winter periods: 1870—71 to 1885—86......		17·00	4·44	0·512	28·25
Mean of 12 summer periods, to 1885		17·04	3·14	0·362	19·91
Mean of 12 winter periods, to 1885—86		17·65	3·58	0·413	23·56
Yearly average for 16 years, to March 31st, 1886..........		33·54	3·81	0·439	47·61
Ditto, excluding the winter 1872—73		33·31	3·25	0·375	40·33
Yearly average for 12 years. to March 31st, 1886		34·69	3·36	0·387	43·47

1873, may have been contaminated with extraneous matter having been suggested. the average of 15½ years, not including this period, is given in the summary.

The amount of chlorides in the rain is nearly always greater in the winter months than in the summer months, although there are some irregularities, which, having been greatest in the first four years of the determinations, the mean of the last 12 years, 1874—1885, is separately given. The excess in the winter months is partly due to the greater amount of chlorides volatilised by the combustion of fuel.

The only published determinations of the amount of chlorides in rain-water, collected at any one locality over any length of time, are those of Lawes, Gilbert, and Warington, see "New Determinations of Ammonia, Chlorine, and Sulphuric Acid in the Rain-water collected at Rothamsted" (*J. Roy. Agric. Soc. Eng.*, 1883 [2], **19**, 313). At Rothamsted, monthly determinations of chlorine in rain-water have been made since June, 1877, and in the above-named paper the results of six years monthly determinations are given. The general average is 1·99 chlorine per million of water, with a mean rainfall of 33·15 inches, equivalent to 24·59 lbs. of common salt per acre. At Rothamsted during the summer months, the amount of chlorides is less than one-half of that of the winter months.

At Rothamsted, and still more obviously at Cirencester, the amount of chlorides brought down during each year in the rain is in excess of that contained in the annual produce of most farm-crops. It has been found at Rothamsted that the amount of chlorides in the drainage from drain-gauges containing unmanured and uncropped soil is almost exactly equal to that contained in the rain.

XIV.—*Some Analogous Phosphates, Arsenates, and Vanadates.*

By JOHN A. HALL, Student in the Laboratory of Owens College.

IN a paper published in the *Journal of the Chemical Society* (Trans., 1885, 353), H. Baker described, among other salts, certain hydrates of trisodium vanadate, viz., $Na_3VO_4,12H_2O$ and $Na_3VO_4,10H_2O$, crystallising in the regular and hexagonal systems; and also $Na_3VO_4,8H_2O$, of which the crystalline form is doubtful.

Baker remarks that the phosphates and arsenates corresponding with the last two had not previously been obtained, and also shows that if solutions of arsenates and phosphates be substituted for a solution of the vanadate, crystals are produced which exhibit the characteristic form of the vanadate. Hence the existence of the salts, $Na_3PO_4,10H_2O$ regular, and $Na_3AsO_4,10H_2O$ regular, as well as of two other salts of a lower but somewhat uncertain degree of hydration, may with great probability be assumed.

To place the question beyond doubt, I undertook the preparation and analysis of these salts, to which I add a description of the orthovanadate of the lowest degree of hydration, the composition of which was left doubtful by Baker.

The following is a summary of the results obtained. The salt first described is $Na_3AsO_4,10H_2O$, regular; the corresponding phosphate could not be obtained. The vanadate described by Baker as $Na_3VO_4,8H_2O$ has been prepared in considerable quantity, but turns out to be a heptahydrated salt, viz., $Na_3VO_3,7H_2O$. The corresponding phosphate, $Na_3PO_4.7H_2O$, was also prepared, but attempts to obtain the arsenate with this degree of hydration failed, a lower hydrate having the formula $Na_3AsO_3,4\frac{1}{2}H_2O$ being formed. No phosphate or vanadate corresponding with this could be produced.

I. *Sodium Arsenate*, $Na_3AsO_4,10H_2O$, *Regular*.

A number of experiments were made with aqueous solutions of trisodium arsenate, $Na_3AsO_4,12H_2O$, and caustic soda, which led to the following as the method for the preparation of the salt.

100 grams of common sodium arsenate is dissolved in 150 c.c. of a solution of caustic soda (1 of soda to 1 of water), the mixture contained in a small beaker is heated to its boiling point, and then placed in a larger one holding as much glycerol as is necessary to bring its level a little higher than that of the solution in the inner beaker. The beakers are covered, placed on a water-bath, and kept at a temperature of 77°, until a sufficient quantity of crystals has been formed (10 hours usually suffice). The mother-liquor is quickly poured off, and the crystals repeatedly treated with hot strong caustic soda solution, finally with alcohol, and kept under alcohol or benzene. By the above method, the difficulty of the complete removal of the mother-liquor (which easily solidifies) from the crystals was overcome, as also the decomposition of the crystals with the formation of the common arsenate, which at once occurs when they are brought into contact with water or dilute alcohol. The salt effloresces in dry air, melts at 85°, and crystallises in the same form as the corresponding vanadate (regular).

In the analysis of this salt, it was found convenient to remove the arsenic acid by ignition with acid ammonium sulphate, when sodium sulphate quite free from arsenic is left.

	Calculated for $Na_3AsO_4,10H_2O$.	Found. Prep. I.	Found. Prep. II.
H_2O	46·39	46·7	46·4
Na_2O	23·96	—	25·0
As_2O_5	29·63	28·2	29·1

A large number of experiments were made with the object of preparing a sodium phosphate corresponding with the decahydrated arsenate and vanadate, but without success. If to an aqueous solution of sodium phosphate and caustic soda, such as would yield on crystallisation at say 70° the salt having 12 mols. H_2O, a little more caustic soda be added, a heptahydrated salt is obtained.

An attempt was made to prepare the decahydrated salt by growing crystals of the corresponding arsenate in a solution of sodium phosphate and caustic soda, but without result.

II. *Sodium Vanadate*, $Na_3VO_4,7H_2O$.

This salt is prepared by allowing a solution of 10 grams of sodium vanadate ($Na_3VO_4,12H_2O$) in 10 c.c. of caustic soda solution (prepared by dissolving 75 grams of caustic soda in 100 c.c. of water) to crystallise at 78°.

The crystals are washed in a manner similar to that used in the preparation of the arsenate. The numbers obtained in the first analysis of this salt were not satisfactory, and a careful microscopic examination of the crystals showed the existence of interstices filled with liquid. The freshly prepared crystals were, therefore, powdered under alcohol before analysis. The following is the method of analysis employed:—The water was determined by loss on ignition, the vanadium by reduction with sulphur dioxide, and titration with potassium permanganate solution. The sodium was estimated as sulphate as follows:—The vanadium was precipitated as silver vanadate, the excess of silver removed by hydrochloric acid, and the filtrate after evaporation heated in a platinum crucible with strong sulphuric acid, ignited, and weighed as sodium sulphate.

	Calculated for		Found.		
	$Na_3VO_4,8H_2O$.	$Na_3VO_4,7H_2O$.	Prep. I.		Prep. II.
H_2O....	43·84	40·6	41·59	41·4	40·9
Na_2O...	28·35	29·97	—		30·7
V_2O_5...	27·81	29·42	28·58	28·75	29·6

These determinations show that the salt contains 7 mols. H_2O, a conclusion supported by the existence of the phosphate next described.

III. *Sodium Phosphate*, $Na_3PO_4,7H_2O$.

Experiments were made with sodium phosphate in the same manner as with sodium arsenate. The following method for the preparation of this salt was employed. 100 grams of common sodium phosphate are added to 100 c.c. of a solution of caustic soda in its own weight of water. The mixture on heating, as in the case of the arsenate previously described, yields crystals of the above phosphate. The crystals thus obtained are generally small; they can be kept under alcohol or benzene. In dry air, they lost water to the extent of 3·8 per cent. in 18 hours and 5·4 per cent. in 48 hours.

The analysis was made in the usual way.

	Calculated for $Na_3PO_4,7H_2O$.	Found.		
		Prep. I.	Prep. II.	
H_2O	43·44	42·6	41·98	43·3*
Na_2O	32·06	32·1	32·5	—
P_2O_5	24·48	22·8	24·3	—

Experiments were made with the object of preparing a heptahydrated arsenate but without success, the solutions always yielding fine crystals of a salt having the composition $Na_3AsO_4,4\frac{1}{2}H_2O$, or $2Na_3AsO_4,9H_2O$.

IV. *Sodium Arsenate*, $Na_3AsO_4,4\frac{1}{2}H_2O$.

This salt can be prepared by allowing a solution of 25 grams of sodium arsenate in 10 c.c. of caustic soda solution prepared as before, to crystallise at a temperature somewhat above 86°.

The crystals were washed and analysed, as in the case of the arsenate previously mentioned.

	Calculated for $Na_3AsO_4,4\frac{1}{2}H_2O$.	Found.		
		Prep. I.	Prep. II.	Prep. III.
H_2O	28·0	27·2	27·3	27·26
Na_2O......	32·1	—	—	32·3
As_2O_5	39·8	—	—	39·7

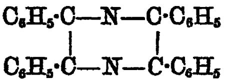
Attempts to prepare the corresponding phosphate and vanadate were unsuccessful. No evidence of lower hydrates than the above described, viz., those with 7 mols. H_2O, could be met with.

* By ignition with lead oxide.

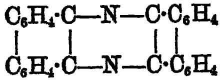
XV.—*On some Azines.*

By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

In a recent communication (Trans., 1886, 826), it was suggested by one of us, in conjunction with Dr. W. H. Wilson, that the compound $C_{28}H_{20}N_2$, obtained from benzoïn and ammonia, and the compound $C_{28}H_{16}N_2$, obtained from phenanthraquinone and ammonia, were related in the manner expressed by the (partially-developed) formulæ—



Ditolane-azotide.

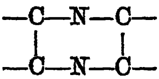


Diphenanthrylene-azotide.

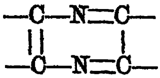
and the nature of this relation was further denoted by the names *ditolane-azotide* and *diphenanthrylene-azotide.*

An experimental proof of this relation was subsequently furnished (Japp and Burton, Trans., 1886, 843) by the conversion of ditolane-azotide, with elimination of hydrogen, into diphenanthrylene-azotide, when the former compound was distilled over heated soda-lime.

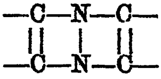
In the above formulæ the distribution of the unsatisfied affinities in the closed-chain complex—



has been left undecided. This complex might either have the constitution—



in which case the compounds would belong to the class of the ketines (see Œconomides, *Ber.*, 19, 2524); or it might be formulated—



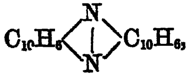
when the compounds would have to be regarded as azines.

In the present communication, we shall endeavour to show that the latter view is correct.

In the first place, assuming that ditolane-azotide is a ketine, it ought to be possible to obtain this compound by the action of nascent hydrogen upon Wittenberg and V. Meyer's benzil-hydroxime[*]:—

$$2C_6H_5{\cdot}C(N{\cdot}OH){\cdot}CO{\cdot}C_6H_5 + 3H_2 = C_{28}H_{20}N_2 + 4H_2O.$$

We therefore prepared the hydroxime and reduced it with tin and hydrochloric acid, but, as the compound formed was in every way distinct from ditolane-azotide, it was not further examined. This negative result appeared to render it improbable that ditolane-azotide was a ketine.

In the meantime, however, an investigation was published by O. N. Witt, which promised to throw light on the constitution of these compounds. Witt has prepared (*Ber.*, **19**, 2794) *αβ-naphthazine*,  $C_{10}H_6\left\langle\begin{matrix}N\\ |\\ N\end{matrix}\right\rangle C_{10}H_6$, by the condensation of β-naphthaquinone with αβ-diamidonaphthalene, an application of Hinsberg's quinoxaline reaction.[†] He further shows that this compound is identical with Laurent's "naphthase," the latter having the formula $C_{20}H_{12}N_2$, instead of the formula $C_{20}H_{14}N_2$, hitherto assigned to it.

Now, between this αβ-naphthazine and diphenanthrylene-azotide, there is a very marked resemblance in properties. Both are substances of high melting point, volatile at a high temperature without decomposition, and sparingly soluble in most solvents. With concentrated sulphuric acid, naphthazine gives a violet solution which changes to orange on gradual dilution with water, whilst still further dilution precipitates the original compound. Diphenanthrylene-azotide behaves with concentrated sulphuric acid in a precisely similar manner, except that the solution in the concentrated acid is deep-blue instead of violet; the change to orange and the subsequent precipitation occur in this case also.

αβ-Naphthazine stands to β-naphthaquinone in the same relation as diphenanthrylene-azotide stands to phenanthraquinone:—

β-Naphthaquinone	$C_{10}H_6O_2$.
αβ-Naphthazine	$C_{20}H_{12}N_2$.
Phenanthraquinone	$C_{14}H_8O_2$.
Diphenanthrylene-azotide	$C_{28}H_{16}N_2$.

Both phenanthraquinone and β-naphthaquinone contain the CO·CO-group. Phenanthraquinone, when heated with ammonia, yields, among other products, diphenanthrylene-azotide. It seemed to us, therefore, that if we could succeed in synthesising αβ-naphthazine from β-naphthaquinone and ammonia, the parallelism between diphenanthrylene-azotide and αβ-naphthazine would be complete, and we should be justified in classing diphenanthrylene-azotide, and also its analogue ditolane-azotide, with the azines:—

---

[*] *Cf.* Ceresole and Koeckert, *Ber.*, **17**, 820.

[†] Hinsberg's "quinoxalines" are, as Witt shows, in all probability azines, whilst the constitution ascribed by Hinsberg to the "quinoxalines" is in reality that of the ketines.

$$\underset{\text{Phenanthraqunone.}}{2C_{14}H_8O_2} + 2NH_3 = \underset{\text{Diphenanthrylene-azotide.}}{C_{28}H_{16}N_2} + 3H_2O + O$$

$$\underset{\beta\text{-Naphthaqunone.}}{2C_{10}H_6O_2} + 2NH_3 = \underset{\alpha\beta\text{-Naphthazine.}}{C_{20}H_{12}N_2} + 3H_2O + O$$

Instead of heating the β-naphthaquinone in sealed tubes with alcoholic ammonia, we adopted the process described on a former occasion (Trans., 1886, 829) in connection with the preparation of ditolane-azotide and diphenanthrylene-azotide, and fused the β-naphthaquinone with ammonium acetate. (For the details of the process, see *loc. cit.*) The product of the reaction was a black friable mass, which was powdered and washed with boiling water. The smallest trace of this substance gave with concentrated sulphuric acid an intense violet coloration, indicating the presence of the desired αβ-naphthazine. By sublimation, needle-shaped crystals of this compound were obtained, which gave the sulphuric acid reaction, the violet changing to orange on gradual dilution; a tarry substance distilled, however, at the same time, rendering the purification of the sublimate a matter of difficulty. We therefore adopted a process of sublimation which had on a previous occasion yielded excellent results in the case of diphenanthrylene-azotide. The crude product was mixed with a small quantity of powdered soda-lime and distilled over a short layer of granulated soda-lime, heated just sufficiently to keep the distillate from condensing in it. The part of the tube containing the mixture was not heated more than was necessary to volatilise the substance, so as to reduce to a minimum all decomposition of the substance by soda-lime. In this way, the tar was retained by the soda-lime, and a yellow sublimate was obtained from which a small quantity of a greenish oily matter was removed by boiling it with alcohol. As Witt's method of purification by recrystallising from boiling naphthalene is somewhat inconvenient, we employed, instead of the naphthalene, a coal-tar oil boiling between 160—180°, which at its boiling point readily dissolved the substance, and on cooling deposited it in tufts of pale-yellow needles, which were washed, first with benzene and afterwards with hot alcohol. This process of purification was twice repeated. The substance, thus purified, melted constantly at 275°, sublimed in thin yellow needles, and was very sparingly soluble in alcohol, the alcoholic solution showing a violet fluorescence. In all these particulars, the behaviour of the compound agreed with Witt's description, except as regards the melting point, which Witt gives as 275°. The substance also showed the sulphuric acid reaction already mentioned.

The yield of αβ-naphthazine by the above method is very small.

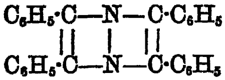
Analysis of the substance dried at 140° gave the following results:—

I. 0·1134 gram substance gave 0·3551 gram CO_2 and 0 0455 gram H_2O.

II. 0·0751 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14·5° and under 372·5 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 14·8° and under 334·5 mm. pressure.

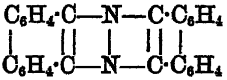
	Calculated for $C_{20}H_{12}N_2$.		Found.	
			I.	II.
C_{20}......	240	85·71	85·40	—
H_{12}.....	12	4 29	4·45	—
N_2......	28	10·00	—	10·18
	280	100·00		

The two compounds—ditolane-azotide and diphenanthrylene-azotide—are therefore to be classed as azines, and in accordance with this view we propose to change the names to *tetraphenyl-azine* and *tetraphenylene-azine.* The relation of the two compounds to each other is expressed by the formulæ—



$$\begin{array}{c}C_6H_5{\cdot}C—N—C{\cdot}C_6H_5\\ \quad\ \ \| \quad\ \ | \quad\ \ \| \\ C_6H_5{\cdot}C—N—C{\cdot}C_6H_5\end{array}$$

Tetraphenyl-azine
(Ditolane-azotide).



$$\begin{array}{c}C_6H_4{\cdot}C—N—C{\cdot}C_6H_4\\ | \quad\ \ \| \quad\ \ | \quad\ \ \| \quad | \\ C_6H_4{\cdot}C—N—C{\cdot}C_6H_4\end{array}$$

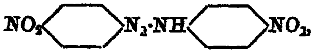
Tetraphenylene-azine
(Diphenanthrylene-azotide).

Normal School of Science,
South Kensington.

XVI.—*Researches on the Constitution of Azo- and Diazo-derivatives.*
I. *Diazoamido-compounds.*

By RAPHAEL MELDOLA, F.R.S, Professor of Chemistry, and F. W. STREATFEILD, Demonstrator of Chemistry, in the Finsbury Technical College, City and Guilds of London Institute.

IN a paper recently communicated to the Chemical Society (Trans., 1886, 624),* we showed that the hydrogen-atom in the —N_2·NH— group of diazoamido-compounds could be readily displaced by alkyl radicles, and we described the ethyl-derivative, paradinitrodiazoamidobenzene, as a type of the class of derivatives thus formed. In the present communication, we give the results of the extension of our experiments to other diazoamido-compounds, these experiments having been undertaken with the hope of being able to throw some light upon the mechanism of the reaction which takes place when these substances are decomposed by acids. Among the points raised in connection with this decomposition was that of a possible intramolecular rearrangement in the —N_2·NH— group on treating the compounds with hydrochloric acid (*loc. cit.*, p. 630). A glance at the formula of the dipara-derivative described in the last paper, viz.,



will suffice to show that this question could not be decided by the decomposition of such a substance, since, the two sides of the molecule being symmetrical, we have no means of identifying among the products of decomposition the particular benzene rings attached respectively to the —N_2— and the —NH— groups. Our first experiments have therefore been directed to the preparation of mixed unsymmetrical diazoamido-compounds in which the two halves of the molecule could be identified after decomposition.

I. *Action of Diazotised Metanitraniline upon Paranitraniline.*

Metanitraniline (1 mol.) was dissolved in the necessary quantity of dilute hydrochloric acid and diazotised by adding a solution of sodium nitrite (1 mol.) to the cold solution. The solution of the diazochloride was then added to a cold dilute solution of paranitraniline hydrochloride (1 mol.). A bright yellow precipitate at once commenced to separate; after being allowed to stand for 12 hours, this was collected, washed with cold water till free from acid, and purified by crystallisation from alcohol, in which it is somewhat more soluble than the isomeric paradinitro-compound. By slow crystallisation from an alcoholic solution, the pure substance was obtained in the form of yellow needles melting at 211° with slight decomposition. The following results were obtained on combustion:—

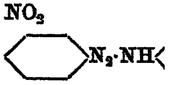
---

* Since the publication of this paper, Dr. Griess has been good enough to point out that one of the compounds described by us, viz, paradinitrodiazoamidobenzene, was obtained by him 24 years ago (*Annalen*, 121, 271).

I. 0·1568 gram dried at 100° gave 0·2892 gram CO_2 and 0·0460 gram OH_2.
II. 0·1048 gram dried at 100° gave 0·1916 gram CO_2 and 0·0301 gram OH_2.
III. 0·0786 gram burnt in a vacuum with CuO gave 16·9 c.c. N at 16·5° and 738·4 mm. bar.
IV. 0·1120 gram burnt in a vacuum with CuO gave 24·2 c.c. N at 17·5° and 736·4 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$.	Found. I.	II.	III.	IV.
C......	50·17	50·30	49·86	—	—
H......	3·13	3·25	3·19	—	—
N......	24·39	—	—	24·28	24·22

In its general properties, the substance resembles the isomeric paradinitro-compound, but it is not quite so acid in character, being less soluble in hot aqueous alkaline solution. The solution in caustic potash or soda is not of such a pure magenta-red, but is somewhat more orange in shade than is the case with the isomeride. According to its mode of formation, its formula might be written—



On this point we shall, however, have more to say in a subsequent part of the paper. We have not thought it necessary to study the products of complete reduction, as these would be in all probability a mixture of meta- and para-phenylenediamines,* and would not be of much importance in the present inquiry.

Decomposition by Hydrochloric Acid.

Some of the substance was sealed up in a glass tube with excess of strong hydrochloric acid, and heated in a water-bath for two hours. On opening the tube, nitrogen was given off and the hydrochloric acid solution was filtered in order to separate a dark tarry residue. The latter, on steam distillation, gave an oily distillate which on standing slowly solidified to a crystalline mass intermixed with oil. The crystals, after purification by pressure between filter-paper and crystallisation from alcohol, were identified as paranitrochlorobenzene (m. p. 83°), and the oil on further examination proved to be a mixture of meta- and para-nitrochlorbenzenes.* The pitchy residue left after steam distillation was uncrystallisable and contained no phenolic substance. The hydrochloric acid solution separated from the tarry residue was found to contain a mixture of para- and meta-nitranilines which were separated by fractional crystallisation from water, the paranitraniline being identified by its melting point, while the metanitraniline, which was left in the solution after the removal of the other modification, was identified by reduction to metaphenylenediamine and then applying the nitrous acid test ("Bismarck Brown") and diazobenzene chloride (chrysoïdine).

---

* Since writing the above, we have satisfied ourselves that this is really the case, by complete reduction and subsequent oxidation, according to the method described further on in this paper. The colour reactions characteristic of a mixture of meta- and para-diamines are immediately shown.

Identification of a Mixture of Meta- and Para-diamines.—We may here mention that in subsequent experiments where a mixture of meta- and para-nitranilines or alkyl-nitranilines was obtained by the decomposition of the compounds under investigation, the most certain and rapid means of identification was found to be that of reduction to the corresponding diamines and the subsequent oxidation of the mixture. A mere trace of one of the diamines in admixture with the other modification reveals itself by the formation of a deep blue or violet colour ("indamine" series) (O. N. Witt, this Journal, Trans.,

---

* It was found by experiment that when a mixture of para- and meta-nitrochlorobenzenes containing an excess of the latter is fused under water, it forms an oil which remains fluid for days. The persistent presence of an oil in the above-mentioned steam distillate, led us at first to suspect the presence of nitrobenzene amongst the products of decomposition, and a method of separating this substance from the nitrochlorobenzenes was therefore devised, which may be worth mentioning here, although it led to the conclusion that no nitrobenzene was present among the products examined. The method in question consists in reducing the mixture of nitrobenzene and nitrochlorobenzenes dissolved in alcohol with tin and hydrochloric acid, evaporating off the alcohol and precipitating the tin by sulphuretted hydrogen. The solution of the hydrochlorides of the bases is then evaporated to dryness and acetylated by means of acetic anhydride and sodium acetate. The acetyl-derivatives, after being washed and dried, are nitrated by being dissolved in strong sulphuric acid in the cold, and the sulphuric acid solution gradually dropped into a well-cooled mixture of nitric and sulphuric acids. The nitro-compounds are thrown out by dilution with water, washed, and hydrolysed by boiling with caustic soda solution. Nitraniline (para) can then be separated from the nitrochloranilines, which are not basic, by means of warm dilute hydrochloric acid, and after precipitation is identified by its melting point and other properties.

1879, 356; *Jour. Chem. Soc. Ind.*, 1882, 255; Bindschedler, *Ber.*, 1880, 207; Nietzki, *Ber.*, 1883, 464; Nölting and Collin, *Ber.*, 1884, 267; Schweitzer, *Ber.*, 1886, 150), passing into red on boiling. In order to apply this test, the hydrochloric or acetic acid solution of the nitroamines is treated with zinc-dust till complete reduction has taken place; ammonium carbonate is then added and the solution boiled and filtered. The filtrate is slightly acidified with acetic acid, and potassium chromate solution added, when the blue colour is immediately developed if both modifications are present, and on boiling the colour changes to red. This method is far more rapid and satisfactory than that of fractional crystallisation of the mixed nitroamines. In the case of meta- and para-nitranilines, for example, it was found by experiments on mixtures of these two isomerides, that with certain proportions an easily fusible compound is formed which is oily under boiling water, and which caused some trouble during our first examination of the basic products of decomposition of the present dinitrodiazoamido-compound. Owing to this tendency to form a compound, it is most difficult to separate pure paranitraniline from the mixture by fractional crystallisation from water, and this difficulty is greatly increased when, as in the present case, only a small quantity of the mixed nitro-amines is available for examination.

Ethyl-derivative.

This compound was prepared by digesting the potassium salt of the dinitrodiazoamido-compound dissolved in alcohol with the theoretical quantity of ethyl iodide, according to the method described in our previous paper (Trans., 1886, 630). Ethylation takes place very readily, and the ethyl-derivative, after crystallisation from alcohol, was obtained in the form of small yellow needles melting at 148° and at the same time frothing up and decomposing. The following are the results of analysis:—

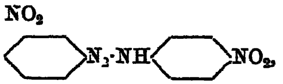
I. 0·1453 gram gave 0·2836 gram CO_2 and 0·0564 gram OH_2.
II. 0·0940 gram burnt in a vacuum with CuO gave 18·9 c.c. N at 18·5° and 735·2 mm. bar.

	Calculated for $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(C_2H_5)C_6H_4 \cdot NO_2$.	Found. I.	Found. II.
C	53·33	53·22	—
H	4·12	4·31	—
N	22·22	—	22·39

The substance resembles its isomeride (Trans., 1886, 630) in appearance and general properties. When heated in a sealed tube in a water-bath for three to four hours with excess of strong hydrochloric acid, it decomposes into nitrogen and a tarry substance, whilst basic compounds remain in the acid solution. The tarry matter, like that obtained by the decomposition of the original substance, furnished an oily mixture of meta- and para-nitrochlorobenzenes on steam distillation. The acid solution contained a mixture of ethylmeta- and ethylparanitraniline. The presence of these two modifications was shown by reduction to the corresponding ethyldiamines; the solution on mere exposure to the air becoming rapidly blue, and giving a deep-blue precipitate immediately on the addition of potassium chromate, this colour changing into red on boiling. A solution of the mixed ethyldiamines prepared for comparison possessed all the foregoing properties. With respect to the constitution of the ethyl-derivative, we shall have some remarks to make further on in this paper.

II. *Experiments on the Decomposition of the Diazobenzene Chlorides by Hydrochloric Acid.*

The results obtained on the decomposition of the compound which, from its mode of formation, might be supposed to have the formula—



although in perfect accordance with the results obtained in similar reactions by other investigators (Griess, *Ber.*, 1874, 1619; Nölting and Binder, *Bull. Soc. Chim.*, **42**, 336), are opposed to the idea that the action of hydrochloric acid is of such a simple character as might appear at first sight. The fact that mixtures of para- and meta-nitrochlorobenzene and of meta- and para-nitranilines are obtained certainly points to the conclusion that intramolecular change occurs in the —N_2·NH— group, since the simplest mode of decomposition imaginable leads to the supposition that the chief products of decomposition would be metanitrochlorobenzene and paranitraniline, or, if isomeric transformation is supposed to take place, metanitraniline and paranitrochlorobenzene. It appeared of interest therefore at this stage of the work to study the action of hydrochloric acid on the diazotised nitranilines, *per se*, and in presence of similar and dissimilar nitranilines.

1. Paranitraniline was diazotised in the usual way and heated in a sealed tube in a water-bath with excess of strong hydrochloric acid in the presence of an equal weight of paranitraniline. The products of decomposition were nitrogen and paranitrochlorobenzene.

2. Metanitraniline similarly diazotised and heated in the presence of metanitraniline gave metanitrochlorobenzene.

3. Metanitraniline diazotised and heated with hydrochloric acid in the presence of an equal weight of paranitraniline, gave a mixture of meta- and paranitrochlorobenzenes and of meta- and para-nitranilines.

4. Paranitraniline diazotised and decomposed in the presence of metanitraniline gave the same products as in the last experiment.

It must be observed that in these experiments the heating of the tubes was commenced as soon as possible after the nitranilines had been diazotised and their solutions mixed, an excess of strong hydrochloric acid being always present, so that the diazoamido-compounds did not in any case separate out. The products of decomposition were, however, precisely the same as those obtained from the corresponding diazoamido-compounds, so that these compounds are actually formed as the first stage in the series of reactions which take place in the sealed tubes, or conversely, the diazoamido-compounds are first resolved into their constituents by the acid, and these products of decomposition then react in some manner, at present inexplicable.

III. *Metadinitrodiazoamidobenzene.*

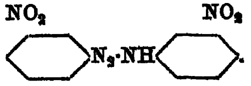
This compound, first obtained by Griess (*Annalen*, 121, 272), was prepared by acting with 1 mol. of $NaNO_2$ upon 2 mols. of metanitraniline in dilute hydrochloric acid solution. The substance separates out as a yellowish-white flocculent precipitate which, after being collected, washed, and crystallised from alcohol, was obtained in the form of straw-coloured needles melting at 194° (195·5° Griess) without decomposition.

I. 0·1066 gram burnt in a vacuum with CuO gave 22·9 c.c. N at 17·5° and 746·7 mm. bar.

II. 0·0889 gram burnt in a vacuum with CuO gave 19 c.c. N at 16·5° and 747·4 mm. bar.

	Calculated for $NO_2\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot NO_2$.	Found.	
		I.	II.
N........	24·39	24·42	24·43

This compound differs from the dipara- and unsymmetrical isomerides in being far less acid in character. It is quite insoluble in hot aqueous alkalis, but dissolves in alcoholic potash and soda with an orange-brown colour; the potassium salt separates out from the solution in alcoholic potash, on cooling, in the form of brown glistening crystals. The constitutional formula of the compound is most probably



According to its mode of preparation, this compound might have been expected to be identical with that described by Hallmann (*Ber.*, 1876, 320), but this is certainly not the case. This author states that his substance melts at 175—176° with decomposition, that it dissolves but sparingly in alcohol, and that it is insoluble in acetic acid, &c. He further states that the substance is not decomposed by heating with hydrochloric acid, even at 130°, in a sealed tube, and that it possesses none of the characters of a diazo-compound. Our substance, besides differing in its melting point, is fairly soluble in alcohol, and readily soluble in acetic acid; it is, moreover, easily decomposable by hydrochloric acid, even at ordinary atmospheric pressure, on heating with strong acid, and more completely at 100° in a sealed tube. The products of decomposition are metanitrochlorobenzene and metanitraniline; no phenolic substance appears to be formed. Hallmann obtained his compound as a residue formed during the diazotising of metanitraniline in a dilute nitric acid solution, and in order to see whether the use of nitric instead of hydrochloric acid would influence the nature of the product we repeated the experiment with this variation, but the only result was a smaller yield of the same product as that obtained in our first experiment. By working in an alcoholic solution as recommended by Hallmann, we have obtained a small quantity of a reddish-brown substance, melting at 175—176°, and agreeing in its properties with the compound described by that author. This, as he suggests, is most probably an amidoazo-compound, and we hope to be able to resume its examination on a future occasion.

Metadinitrodiazoethylamidobenzene, $\underset{(1)}{NO_2\cdot C_6H_4}\cdot \underset{(3)}{N_2}\cdot \underbrace{N(C_2H_5)}_{(3)}\cdot C_6H_4\cdot \underset{(1)}{NO_2}$

This compound was prepared from the foregoing by the action of ethyl iodide on the potassium salt, according to the method already described. After crystallisation from alcohol, it forms small opaque whitish-yellow needles, melting at 119°.

0 1435 gram gave 0·2809 gram CO_2 and 0·0508 gram OH_2.

	Calculated.	Found.
C	53 33	53·38
H	4·12	3·93

This ethyl-derivative on decomposition by hydrochloric acid, gives ethylmetanitraniline and metanitrochlorobenzene.* The former compound was identified by its melting point (59—60°), and by conversion into its nitrosamine (m. p. 47°). Both these compounds have been recently prepared by Nölting and Stricker (*Ber.*, 1886, 546).

---

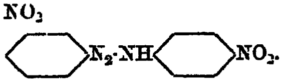
* This decomposition can be effected at ordinary pressure by simply boiling with strong hydrochloric acid in a flask, and furnishes a ready method of preparing pure ethylmetanitraniline.

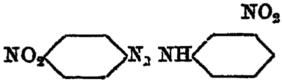
IV. *The Identity of Mixed Diazoamido-compounds.*

Since the original discovery by Griess of the interesting fact that the compound formed by combining diazotised bromaniline with aniline is identical with that obtained by combining diazotised aniline with bromaniline (*Ber.*, 1874, 1619), it has been generally admitted that mixed diazoamido-compounds of the type $X{\cdot}N_2{\cdot}NH{\cdot}Y$ are identical, whether X or Y be diazotised first. In addition to the instance quoted, Griess also gives the following:—The diazoamido-compound formed by the action of diazobenzene on toluidine is identical with that formed by the action of diazotoluene on aniline; the compound formed by the action of diazobenzene on amidobenzoic acid is identical with that formed by the action of diazobenzoic acid on aniline. The identity of these compounds is shown not only by their similarity in physical properties, but also by their giving the same products on decomposition, and Sarauw has shown that they give similar products on treatment with phosgene (*Ber.*, 1881, 2442). Additional confirmation of these results is given by Nölting and Binder (*Bull. Soc. Chim.*, 1884, **42**, 336). Whether a similar identity exists among the secondary diazoamido-compounds obtained by combining tetrazo-salts with amines, and the converse, has not yet been established.

In accordance with the foregoing statements, it might have been anticipated that the compound obtained by acting on metanitraniline with paranitrodiazobenzene chloride would be identical with that obtained by combining metanitrodiazobenzene chloride with paranitraniline, *i.e.*, with the compound described in the previous portion of this paper. This anticipation has been confirmed by experiment. On mixing a solution of diazotised paranitraniline with a dilute solution of metanitraniline hydrochloride, a copious yellow precipitate slowly separates, and this, after purification, forms yellow needles melting at 211°, and giving on decomposition with hydrochloric acid a mixture of meta- and para-nitrochlorbenzenes, and of meta- and para-nitranilines. Its ethyl-derivative melts at 148°, and gives, on decomposition with hydrochloric acid, a mixture of the two nitrochlorobenzenes and the two ethylnitranilines, thus fully establishing the identity of this compound with that previously described.

According to the mode of formation of these compounds, two formulæ are possible, viz.:—

I. 

II. 

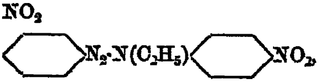
Isomeric transformation must thus occur in one or the other method of preparation, and the decision between the two formulæ would therefore lead to the important conclusion as to which nucleus the N_2-group became finally attached. To throw further light on this point we have studied the action of the diazotised nitranilines on the ethylnitranilines.

(1.) *Action of Diazotised Metanitraniline on Ethylparanitraniline.*—Metanitraniline (1 mol.) was diazotised in the usual way, and the solution mixed with the necessary quantity of ethylparanitraniline* dissolved in dilute hydrochloric acid. After standing for about 14 hours, a copious yellow precipitate had formed; this was collected, washed with water till free from acid, and then the water displaced by alcohol. After crystallisation from boiling alcohol, in which the substance is very sparingly soluble, it was obtained in the form of yellow needles, melting at 174—175°.

0·1954 gram gave 0·3824 gram CO_2 and 1·0770 gram OH_2.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2$.	Found.
C	53·33	53·37
H	4·12	4·37

This compound is accordingly isomeric with that of melting point 148° described in the previous part of this paper. Its constitutional formula is in all probability



this formula corresponding with that of the ethyl-derivative of No. I. When heated in a sealed tube in a water-bath with strong hydrochloric acid, this substance decomposes, with the formation of ethylparanitraniline and metanitrochlorobenzene, thus differing from its isomeride of melting point 148°, which under these circumstances gives a mixture of the two nitrochlorobenzenes and the two ethylnitranilines. On complete reduction and oxidation, it gives the intense blue colour characteristic of the "indamines."

---

* The ethylparanitraniline employed in these experiments was obtained by the decomposition of the ethyl derivative of paradinitrodiazoamidobenzene by hydrochloric acid. It was purified by conversion into its nitrosamine, and the latter, after crystallisation from alcohol, was decomposed by cohobation with hydrochloric acid and alcohol. Ethylmetanitraniline was prepared in a similar way from metadinitro-diazoethylamidobenzene.

(2.) *Action of Diazotised Paranitraniline on Ethylparanitraniline.*—On mixing the solutions in the usual way, a bulky yellow precipitate separated, which, after crystallisation from alcohol, was obtained in the form of small yellow needles melting at 192°, and identical with the paranitrodiazoethylamidobenzene described in our previous paper (Trans., 1886, 630).

(3.) *Action of Diazotised Paranitraniline on Ethylmetanitraniline.*—The yellow precipitate formed on allowing the mixed solutions to stand was purified by crystallisation from alcohol, in which it dissolves but sparingly, and then formed orange-yellow needles, melting at 187°. The appearance and properties of this substance show that it is probably an amidoazo-compound, possibly having the formula

$$\underset{(1)}{\mathrm{NO_2}}\cdot\mathrm{C_6H_4}\cdot\underset{(4)}{\mathrm{N_2}}\cdot\mathrm{C_6H_3}\cdot\underset{(3)}{\mathrm{NO_2}}\cdot\underbrace{\mathrm{NH(C_2H_5)}}_{(1)}.$$

Under no conditions have we been as yet able to obtain a diazoethylamido-compound by the action of diazotised paranitraniline upon ethylmetanitraniline. The crude precipitate is always contaminated with a certain quantity of paradinitrodiazoamidobenzene, which can be dissolved out by treatment with alcoholic potash, and the compound thus left, after being crystallised from alcohol, is quite different in appearance from any of the diazoethylamido-derivatives which we have prepared. The distinct tinctorial properties of this substance, taken in conjunction with the fact that its melting point is considerably higher than that of the unsymmetrical compound

$$\underset{(1)}{\mathrm{NO_2}}\cdot\mathrm{C_6H_4}\cdot\underset{(3)}{\mathrm{N_2}}\cdot\underbrace{\mathrm{N(C_2H_5)}}_{(4)}\cdot\mathrm{C_6H_4}\cdot\underset{(1)}{\mathrm{NO_2}},$$

obtained in the foregoing experiment (1), make it extremely probable that we have here a true amidoazo-compound, and we propose to submit this substance to further investigation.

(4.) *Action of Diazotised Metanitraniline upon Ethylmetanitraniline.*—The solutions were mixed as before, and gave on standing an ochreous resinous-looking deposit, which, after washing with water and crystallisation from alcohol, presented the appearance of small opaque whitish-yellow needles melting at 119°, and thus identical with the compound already described as being obtained by the direct ethylation of metadinitrodiazoamidobenzene.

The precise significance of these experiments will be considered subsequently. It may be here remarked, with reference to the product obtained in Experiment 3, that the ethylnitraniline (meta) having the para-position with respect to the $NH{\cdot}C_2H_5$-group open, offers every facility for the formation of an amidoazo-compound. We have made some preliminary experiments with this substance in order to see in what respects it differs from its isomeride of m. p. 174—175°, obtained by the action of diazotised metanitraniline on ethylparanitraniline, and we find that on complete reduction and oxidation, it gives a violet colour very distinct from the pure blue of the "indamine" reaction, as given by the reduction and oxidation of the other ethyl-derivatives. This colour may arise from the oxidation of a mixture of paradiamidobenzene and ethyltriamidobenzene, but this point will require further investigation. The substance is readily decomposed by acids, but we have not as yet examined the products. If further examination should confirm the view that the substance is an amidoazo-compound, it will have to be classed with the β-naphthylamine azo-derivatives described by one of us (Trans., 1883, 430, and Trans., 1884, 116), which, according to Lawson (*Ber.*, 1885, 796), behave like diazo-compounds when decomposed by acids.

V. *Benzyl-derivatives.*

In order to test the wider applicability of the method described in our previous paper, we have extended our experiments by preparing the benzyl-derivatives of the foregoing diazoamido-compounds. These derivatives are readily formed by boiling the alcoholic solution of the potassium salts with the necessary quantity of benzyl chloride, the only precaution necessary being that the alcoholic solution should not be too dilute, otherwise some of the benzyl chloride is directly decomposed by the alkali, and the yield of benzyl-derivative is correspondingly diminished. The benzylation is generally complete in from two to three hours.

(1.) *Paradinitrodiazobenzylamidobenzene*, formed by the benzylation of the paradinitrodiazoamido-compound, crystallises from alcohol, in which it is but sparingly soluble, in minute yellow needles melting at 187°. The substance dissolves very readily in benzene, and a specimen crystallised from this solvent had a melting point of 190°.

0·0675 gram burnt in a vacuum with CuO gave 10·8 c.c. N at 14·7° and 764·3 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_7H_7){\cdot}C_6H_4{\cdot}NO_2$.	Found.
N	18·57	18·87

On heating with strong hydrochloric acid in a sealed tube in a water-bath for 3—4 hours, decomposition takes place in the same manner as with the ethyl-derivative. The contents of the tube consisted of a clear solution containing silvery laminated crystals and a reddish resinous mass. The crystals consisted of the hydrochloride of benzylparanitraniline, but the greater portion of this substance remained in the insoluble resin, owing to its feebly basic properties. On submitting this resin to steam distillation, paranitrochlorobenzene passed over and the benzylnitraniline was extracted from the residue by warm acetic acid (equal parts glacial acid and water), and crystallised out as the solution cooled.

Benzylparanitraniline, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_7H_7 = 1:4$, after purification by crystallisation from dilute alcohol, forms golden-yellow scales, readily soluble in alcohol and benzene, and melting at 142—143°. It is but very feebly basic, and does not form a platinochloride. The *nitrosamine* was obtained by adding the necessary quantity of sodium nitrite to the solution of the substance in alcohol and dilute hydrochloric acid. On dilution with water, a whitish flocculent precipitate is thrown out, which, after being collected and washed with water, was crystallised from dilute alcohol and then from dilute acetic acid. It forms flat, straw-coloured needles, with a silvery lustre readily soluble in cold alcohol and benzene, and melting at 107·5°.

0·0994 gram burnt in a vacuum with CuO gave 14·1 c.c. N at 16·5° and 752·2 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N(NO)C_7H_7$.	Found.
N	16·34	16·32

(2.) *Metadinitrodiazobenzylamidobenzene.*—This substance, obtained from the corresponding diazoamido-compound, crystallises from its alcoholic solution in pale-yellow needles, which glisten in the mother-liquor with brilliant prismatic colours. It is more soluble in alcohol than the preceding isomeride, and, like the latter, dissolves readily in benzene; its melting point is 142°.

0·1659 gram gave 0·3680 gram CO_2 and 0·0620 gram OH_2.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_7H_7){\cdot}C_6H_4{\cdot}NO_2$.	Found.
C............	60·48	60·49
H	3·97	4·15

On decomposition with hydrochloric acid, it gives metanitrochlorobenzene and *benzylmetanitraniline*. The latter is more basic than the corresponding para-compound, and can be dissolved out from the contents of the tube by warm hydrochloric acid, the hydrochloride separating on cooling in the form of large silvery scales.

The free base, when allowed to crystallise slowly from dilute alcohol, forms magnificent golden-yellow laminæ melting at 107°.

0·1280 gram gave 0·3182 gram CO_2 and 0·0610 gram OH_2.

	Calculated for $NO_2 \cdot C_6H_4 \cdot NH \cdot C_7H_7$.	Found.
C............	68·42	67·79*
H...........	5·26	5·29

The *nitrosamine*, $NO_2 \cdot C_6H_4 \cdot N(NO)C_7H_7 = 1 : 3$, is readily formed on adding sodium nitrite to the solution of the substance in acetic acid, and separates out on dilution with water as a viscid oil, which does not solidify on long standing.

(3.) *Benzyl-derivative of the Unsymmetrical Dinitrodiazoamido-compound.*—In confirmation of the results obtained by the action of ethyl iodide, we have found on careful comparison that the benzyl-derivative of the compound resulting from the action of diazotised metanitraniline on paranitraniline is identical with the benzyl-derivative of the compound obtained by acting on metanitraniline with diazotised paranitraniline. The substance is almost insoluble in alcohol, but dissolves readily in benzene. After several crystallisations from this last solvent, it forms microscopic yellow needles melting at 180°.

0·2067 gram burnt in a vacuum with CuO gave 32·8 c.c. N at 14° and 748·5° mm. bar.

	Calculated for $NO_2 \cdot C_6H_4 \cdot N_2 \cdot N(C_7H_7) \cdot C_6H_4 \cdot NO_2$.	Found.
N............	18·57	18·38

On decomposition by heating with hydrochloric acid, it gives a mixture of benzylpara- and benzylmetanitraniline and the two corresponding nitrochlorobenzenes. The mixed benzylnitranilines readily give the "indamine" reaction on reduction and oxidation.

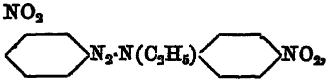
(4.) *Action of Diazotised Metanitraniline on Benzylparanitraniline.*—In order to see whether this compound would be isomeric with the benzyl-derivative referred to in the last experiment, as might have been expected from the previous results with the ethyl-derivatives, diazotised metanitraniline was mixed with an alcoholic solution of benzylparanitraniline containing hydrochloric acid. The results were, however, somewhat unsatisfactory, doubtless owing to the circumstance that the feebly basic properties of the benzylparanitraniline make it necessary to use alcohol as a solvent. The product of the reaction is extremely small and very impure, smelling strongly of nitrochlorobenzene, and probably containing some of Hallman's compound. After being collected and washed with water, it was extracted several times with hot alcohol, and the residue repeatedly crystallised from benzene. The final product consisted of a very small quantity of a substance crystallising in minute yellowish-white opaque needles, mixed with larger ochreous crystals. The melting point was 185°, further purification being prevented by the small quantity of material at our disposal.

---

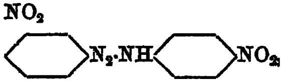
* The low carbon is probably due to the highly electrical properties of the substance, which render it extremely difficult to weigh out without loss.

VI. *Summary of Results and Theoretical Considerations.*

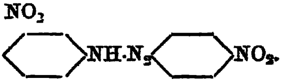
Although at this stage of the investigations it would be premature to attempt to generalise too widely, it nevertheless seems desirable to consider the theoretical bearings of the present experiments, if only for the purpose of putting the facts in a distinct light, so as to clear the ground for the future extension of our researches. The identity of the unsymmetrical compound obtained by the action of diazotised metanitraniline on paranitraniline with that resulting from the action of diazotised paranitraniline on metraniline can only be brought about by the transference of the N_2-group to the position occupied by the NH-group in one or the other method of formation. The ethyl-derivatives obtained in the course of the present investigation enable us to conclude with some degree of probability *that the transference of the* N_2*-group is to the para-position.* This follows from the fact that the ethyl-derivative of m. p. 174—175°, obtained by the action of diazotised metanitraniline on ethylparanitraniline, is isomeric, and not identical with the ethyl-derivative (m. p. 148°) of the unsymmetrical compound prepared by direct ethylation. If, as the appearance and properties of the substance indicate, this 174—175° m. p. ethyl-derivative is a true diazoamido-compound, its formula must be—



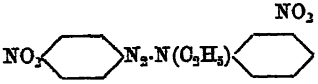
that is to say, it must be an ethyl-derivative of the unknown compound—



and the unsymmetrical compound of m. p. 211° (ethyl-derivative 148°) must therefore have the constitution expressed by the formula—



From this it follows *that when metanitraniline is diazotised and combined with paranitraniline, the* N_2*-group becomes transferred to the paranitraniline half of the molecule.** The one piece of evidence necessary for the direct confirmation of the foregoing conclusion would be the formation of the unsymmetrical ethyl-derivative (m. p. 148°) of which the formula is most probably—



from diazotised paranitraniline and ethylmetanitraniline, but, as already explained, the reaction apparently takes another course in this case, and leads to the production of what seems to be an amidoazo-compound.

With respect to the transference of the N_2-group to the para-position, we may here point out that evidence of a similar nature is to be found in a paper by Nölting and Binder (*Bull. Soc. Chim.*, **42**, 336), although these authors do not state explicitly the inference which may be legitimately drawn from their experiments. Thus, the diazoamido-compound obtained by the action of diazotised aniline on paratoluidine is identical with that resulting from the action of diazotised paratoluidine on aniline, as already pointed out by Griess. When decomposed by bromine, this compound splits up into paradiazotoluene bromide and tribromaniline, from which the authors conclude that it has the constitution—

$$\underset{(1)}{CH_3}\cdot C_6H_4\cdot \underset{(4)}{N_2}\cdot NH\cdot C_6H_5.$$

When aniline is diazotised and combined with paratoluidine, it appears, therefore, that a similar transference of the N_2-group takes place.

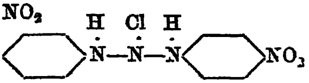
The migration of the N_2-group can perhaps be best explained by adopting the suggestion of Victor Meyer (*Ber.*, 1881, 2447) that an intermediate compound is first formed.† According to this view, the changes which occur when a solution of metanitrodiazobenzene chloride is added to a solution of paranitraniline would be thus represented—

---

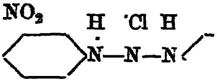
* This conclusion is opposed to that arrived at by Sarauw (*Ber.*, 1882, 46), who states that the NH-group becomes attached to the *more negative* radicle. If this statement held good generally, it might have been expected that the NH-group in the present compound would have been attached to the paranitraniline half of the molecule.

† The formation of unstable additive compounds of the benzene-azonaphthols with hydrogen chloride and hydrogen bromide has been observed by Liebermann, *Ber.*, 1883, 2861.

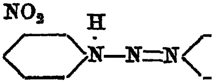
First stage....



Second stage...

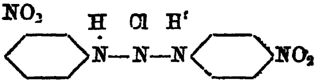


Third stage....

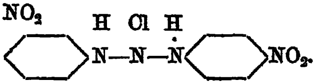


The latter compound, when heated with strong hydrochloric acid, gives a mixture of the two nitranilines and the two nitrochlorobenzenes, so that at a high temperature it must be supposed that the intermediate compound is again formed, and that this splits up in two ways—

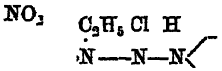
I.



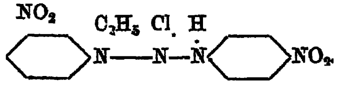
II.



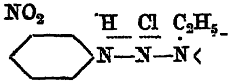
The first mode of decomposition would give a diazoamido-compound, which on decomposition by hydrogen chloride would give paranitrochlorobenzene and metanitraniline, and the second mode of decomposition would similarly lead to the production of metanitrochlorobenzene and paranitraniline. It is not at all improbable that both these reactions go on simultaneously in a sealed tube at 100°. The mixed products obtained by the decomposition of the ethyl- and benzyl-derivatives of the above compound can be accounted for in a similar manner—



II.



In the second mode of decomposition, however, the ethyl chloride is not actually set free, but at the moment of decomposition exchanges C_2H_5 for the hydrogen of the NH-group. On the other hand, when the ethyl-group is already in the more stable para-position, as is the case with the compound of m. p. 174—175°—



the decomposition must be considered to take place in the above more simple manner, the products being, as we have shown, simply ethylparanitraniline and metanitrochlorbenzene.

We propose to test these views by further experimental investigation, and hope soon to be able to resume the study of the supposed amidoazo-compound obtained by the action of paranitrodiazobenzene chloride on ethylmetanitraniline, this compound offering many points of special interest in connection with the present researches.

In concluding, we have to express our thanks to our students Messrs. H. T. Pentermann and W. P. Dreaper, who have materially assisted us by making many of the foregoing analyses.

XVII.—*On the Distribution of the Nitrifying Organism in the Soil.*

By R. Warington.

In a previous communication to the Society (Trans., 1884, 645), an account was given of some experiments made at Rothamsted in 1883 and 1884, to ascertain to what depth the presence of the nitrifying organism could be detected in the soil. The trials were confined to one field on the farm (Agdell), having a stiff clay subsoil. Portions of the soil were removed, with suitable precautions, from the side of a pit, and placed in sterilised solutions of diluted urine (4 c.c. per litre), containing a little calcium carbonate. The subsequent occurrence of nitrification in a solution was taken as proof that the soil introduced contained the nitrifying organism. Working in this way, it was concluded from three series of experiments, embracing 28 trials, "that in our clay soils the nitrifying organism is not uniformly distributed much below 9 inches from the surface. On much slighter grounds, it may perhaps be assumed that the organism is sparsely distributed down to 18 inches, or possibly somewhat further. At depths from 2 feet to 8 feet, there is no trustworthy evidence to show that the clay contains the nitrifying organism. It is however probable that the organism may occur in the natural channels which penetrate the subsoil at a greater depth than in the solid clay. In the case of sandy soils, we may probably assume that the organism will be found at a lower depth than in clay."

A further investigation of the subject has now been made. The new trials were carried out in the years 1885 and 1886. Besides the soil of the field with a clay subsoil, already experimented on, the soil of another field (Great Hoos), having a loamy subsoil, was also investigated. In all, six series of experiments, including 69 trials, have been made. The method employed was the same as that made use of in the earlier experiments, and described in the former communication, with the exception that *now* more soil (about 0·2 gram) was introduced into the trial solutions, and these solutions contained gypsum (0·1 gram per litre), in addition to the urine and calcium carbonate previously employed. The gypsum was added in consequence of the results obtained in another investigation (Trans., 1885, 758), showing that the presence of gypsum greatly facilitates the process of nitrification in the case of urine solutions. The solutions to which soil had been added were kept in a dark cupboard, the temperature being that of the air.

The first experiments to be noticed were made with soils obtained from Great Hoos Field, in which pits were dug for soil-sampling in July and August, 1885. In this field there is no sharp boundary between the surface soil and subsoil; the latter is loamy, and occasionally sandy. The previous summer had been dry; the soils were therefore dry, and towards the surface were found to be considerably disintegrated.

Fallow Soil, Hoos Field, sampled August 1, 1885.—This soil belonged to a plot of alternate wheat and fallow; it was in 1885 without a crop. The depths from which the soil was taken are shown in a subsequent table. Worm-holes were found to extend 2 feet from the surface. The subsoil at 2 and 3 feet was clayey, but that from 4, 6, and 8 feet was sandy.

White Clover Soil, Hoos Field, sampled August 4, 1885.—This plot had grown white clover, manured with ash constituents only, for several years. The roots of the clover were found to extend 3 feet from the surface. The soil near the surface was very dry. The subsoil consisted of clay and sand very irregularly distributed.

Bokhara Clover Soil, Hoos Field, sampled August 4, 1885.—On this plot, Bokhara clover had been grown for several years, and manured as the preceding plot. Only two samples of soil were taken; both were from an invasion of hard chalk, interspersed with a little brown loam, from a depth of about 7 feet from the surface.

Lucerne Soil, Hoos Field, sampled August 14, 1885.—This plot had a similar history to that of the two preceding. The soil was very dry, and towards the surface much disintegrated; the surface soil was full of cavities, and that at 16 inches very crumbly and porous. Worm-holes containing living worms extended 4 feet from the surface.

The roots of the lucerne were seen at 6 feet from the surface, but they did not penetrate the chalk. Chalk occurred at 6 feet from the surface. Both the samples of soil at 8 feet from the surface were from chalk. All the samples taken, down to the chalk, were selected from places in the immediate neighbourhood of lucerne roots.

It is to be noted that a strong breeze was blowing on the day when these samples were taken; and the surface soil being very dry, there was danger of soil-dust entering the sterilised solutions when the bottles containing them were opened for the introduction of the soil. A screen was erected to afford shelter from the wind; but it is impossible to say that the protection from dust was complete.

The urine solutions to which the samples of soil had been added were examined from time to time with diphenylamine, to ascertain if nitrification had commenced: the results of the examinations are shown in the following tables. Solutions in which the nitric acid found was "considerable," were not generally further examined. Samples of soil marked "C" were chalk.

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Hoos Field, Fallow Plot) from various depths on August 1st, 1885.

Depth from which soil was taken.	August 24th (23 days).	September 22nd (52 days).	March 29th (240 days)
9 inches	distinct	large	—
16 " (*a*)	none	considerable	—
" (*b*)	"	considerable	—
2 feet (*a*)	"	considerable	—
" (*b*)	"	considerable	—
3 feet (*a*)	"	none	large
" (*b*)	"	"	none
4 feet (*a*)	"	"	"
" (*b*)	"	considerable	—
6 feet (*a*)	"	none	none
" (*b*)	"	"	"
8 feet (*a*)	"	"	"
" (*b*)	"	"	"

The results yielded by these experiments were in several respects distinctly different from those formerly obtained. The process of nitrification was far more speedy in most of the cases in which it occurred. Soil obtained from very considerable depths was also in many instances found capable of starting nitrification. Soil from the fallow plot was effective without exception down to 2 feet from the surface, and one sample from 3 feet, and one from 4 feet also produced

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Hoos Field, White Clover Plot) from various depths, August 4th, 1885.

Depth from which soil was taken.	August 24th (20 days).	September 22nd (49 days).	March 29th (237 days).
9 inches	moderate	—	—
16 ,, (*a*)	none	considerable	—
,, (*b*)	,,	considerable	—
2 feet (*a*)	,,	considerable	—
,, (*b*)	,,	trace	large
3 feet (*a*)	,,	considerable	—
,, (*b*)	,,	none	large
4 feet (*a*)	,,	,,	distinct
,, (*b*)	,,	,,	none
6 feet (*a*)	,,	,,	,,
,, (*b*)	,,	considerable	—
8 feet (*a*)	,,	none	none
,, (*b*)	,,	,,	,,

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Hoos Field, Bokhara Clover Plot), August 4th 1885.

Depth from which soil was taken.	September 23rd (50 days).	March 29th (237 days).
7 feet (*a*) C	none	none
,, (*b*) C	,,	,,

nitrification. Soil from the white clover plot was effective without exception down to 3 feet, and one sample from 4 feet, and one from 6 feet also proved effective. Soil from the lucerne plot (Table, p. 122) was still more efficacious, all samples down to 4 feet producing nitrification, and one at 6 feet exhibiting the same property.

It seemed doubtful whether the unexpected exhibition of nitrifying power by these subsoils was due to the more favourable character of the solutions in which they were placed, or whether the results were simply the result of contamination of the solutions by soil-dust when the bottles were opened in the field, the surrounding soil having been throughout the taking of the samples unusually dry, and a brisk breeze at times blowing. It was resolved therefore to repeat the experiments under more favourable conditions of weather.

In the spring of 1886, further trials were made, both with the soil of Agdell field, and with that of Great Hoos field. The solutions into

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Hoos Field, Lucerne Plot) from various depths, August 14th, 1885.

Depth from which soil was taken.	September 22nd (39 days).	March 25th (223 days).
9 inches	considerable	—
16 " (*a*)	none	large
" (*b*)	considerable	—
" (*c*)	distinct	large
2 feet (*a*)	none	large
" (*b*)	"	large
" (*c*)	considerable	—
3 feet (*a*)	considerable	—
" (*b*)	none	large
" (*c*)	"	large
4 feet (*a*)	"	large
" (*b*)	"	large
" (*c*)	"	large
6 feet (*a*)	considerable	—
" (*b*) C	none	none
8 feet (*a*) C	"	"
" (*b*) C	"	"

which the soil was introduced consisted, as in the experiments of the preceding year, of dilute urine with gypsum.

Red Clover Soil, Agdell Field, sampled April 16, 1886.—The pit was dug in the unexperimental portion at the south end* of the field. Red clover had been sown the previous year, and had not yet borne a crop; there was a fair plant. Roots were not observed below 27 inches. The surface soil was 6 to 8 inches deep, and was sharply divided from the subsoil. This subsoil consisted generally of a rather loamy clay. The samples were taken in the intervals of a showery day.

Fallow Soil, Hoos Field, sampled May 7, 1886.—This soil was from an unexperimental portion of the same plot which had been examined in 1885. The subsoil down to 2 feet consisted of a friable loam, below this depth it became stiffer. At one side of the pit an invasion of chalk occurred. The weather was fine and calm during the taking of the samples.

The results of the examination of the solutions were as follow:—

---

* In the former paper (Trans., 1884, 648), this part of the field is by a mistake called the north end.

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Agdell Field, cropped with Red Clover) from various depths, April 16*th*, 1886.

Depth from which soil taken.	May 28th (42 days).	June 28th (73 days).	August 3rd (109 days).	Nov 20th (218 days).
6 inches........	considerable	large	—	—
12 "	distinct	large	—	—
18 " (*a*)	none	considerable	large	—
" (*b*)	distinct	large	—	—
27 inches (*a*)	trace	large	—	—
" (*b*)	trace	large	—	—
3 feet (*a*)	none	considerable	large	—
" (*b*)	"	considerable	large	—
4 feet (*a*)	"	none	distinct	considerable
" (*b*)	"	distinct	considerable	large
6 feet (*a*)	"	none	distinct	large
" (*b*)	"	"	none	none

Nitric or Nitrous Acid produced in Dilute Urine with Gypsum, seeded with Soil (Hoos Field, Fallow Plot) from various depths, May 7*th*, 1886.

Depth from which soil taken.	June 11th (35 days).	July 14th (68 days).	August 16th (101 days).	Nov. 20th (197 days).
9 inches........	large	—	—	—
16 " (*a*)	distinct	large	—	—
" (*b*)	trace	large	—	—
2 feet (*a*)	considerable	large	—	—
" (*b*)	large	—	—	—
3 feet (*a*)	considerable	large	—	—
" (*b*)	none	none	considerable	large
4 feet (*a*)	"	"	none	none
" (*b*)	"	"	"	"
5 feet (*a*) C ..	"	"	"	"
" (*b*)	"	"	distinct	large
6 feet	(not tested)	large	—	—

It is evident that these new trials, made under more favourable conditions as to exclusion of soil-dust, confirm the results of the previous year, and afford proof of the distribution of the nitrifying organism to a considerable depth in the subsoil. Taking the whole of the 69 trials, and classifying them according to the depth of the soil experimented on, we obtain the following results. Soil from the depth of 27 inches has been reckoned as 2 feet.

We have thus no failure to produce nitrification in samples of soil down to, and including, a depth of 2 feet from the surface. At 3 feet,

Depth of soil.	Number of trials.	Number of solutions nitrifying.	Number nitrifying out of 10 trials.	
			Including chalk.	Excluding chalk.
Less than 2 feet.	17	17	10·0	10·0
2 feet..........	11	11	10·0	10·0
3 ,, ...	11	10	9·1	9·1
4 ,, ...	11	7	6·4	6·4
5 ,, ...	2	1	5·0	10·0*
6 ,, ...	9	4	4·0	5·0
7 ,, ...	2	0	0·0	—
8 ,, ...	6	0	0·0	0·0

* This result represents a single experiment only.

only one sample out of 11 fails. Below 3 feet, failures become far more numerous, and increase in frequency as the depth increases. At 6 feet, if we exclude the experiment with chalk, one half of the trials resulted in nitrification. At 7 and 8 feet, the soil failed entirely to produce nitrification. The trials at 7 feet were, however, limited to two experiments with chalk; those at 8 feet included four experiments with clay. None of the six trials with chalk resulted in nitrification.

To what cause are we to attribute the production of nitrification by subsoils in these experiments, while subsoils from the same depth, and in one case from the same field, failed entirely to produce nitrification in the earlier experiments. The only apparent explanation is the presence of gypsum in the urine solutions employed in the later experiments. This explanation is probably sufficient. It has been abundantly proved by other experiments that nitrification will not commence if the alkalinity of the ammoniacal solution exceeds 400 parts of nitrogen per million, and that an alkalinity far below this point greatly retards the commencement of nitrification, and may altogether prevent it if a large quantity of the nitrifying organism is not present. It is quite true that the amount of ammonium carbonate produced in a 4 per 1000 urine solution would be very small, and quite insufficient to prevent nitrification if seeding were made with a vigorous nitrifying organism. We may naturally assume, however, that the organism present in a clay subsoil, several feet from the surface, is neither abundant nor vigorous in habit; it may consequently be unable to develop in a decidedly alkaline urine solution. The addition of gypsum to the solution, by neutralising all excess of alkali, removes any hindrance to the development of a feeble organism.

That the nitrifying organism occurring in subsoils is of comparatively feeble power is shown by the greater length of time which a subsoil takes to start nitrification, as compared with a similar quantity of surface soil. It is not possible from the results of these experiments to give the average time required to start nitrification by soils from various depths, the conditions as to temperature, and the frequency of observation, having been very different in the different series of experiments; but it is quite possible to deduce from the results an average order of priority, if we give numerical values to the amounts of nitric acid found at the different dates of the commencement of nitrification. Thus giving the value 1 to a "considerable" quantity of nitric acid found at the *first* examination of the solution, a value 2 for a "distinct" quantity, and a value 3 for a "trace." And again a value of 4 for a "considerable" quantity marking a commencement of nitrification at the *second* examination, a value 5 for a "distinct" quantity, and a value 6 for a "trace." And proceeding in the same order with commencements of nitrification occurring at a *third* examination, we are able finally to obtain the average order of priority in commencement of nitrification for each depth of soil.*

Order of Priority in commencement of Nitrification in Solutions seeded with Soil from different depths.

Depth of soil	9 ins.	16 ins.	2 ft.	3 ft.	4 ft.	5 and 6 ft.
Number of solutions nitrifying ...	6	11	11	10	7	5
Average order of priority in nitrification	1·33	3·36	3·73	4·90	6·57	5·00

We observe at once a great difference between the activity of soil 9 inches, and soil 16 inches in depth; and below this depth the activity of the soil continues gradually to diminish. The figures do not, however, afford a perfectly smooth order, those belonging to a depth of 4 feet being apparently rather high, and those for 5 and 6 feet rather low.

The general result of the experiments is thus to indicate that although the nitrifying organism may occur at a considerable depth in a subsoil of loam or clay, it occurs there in small quantity and in feeble condition.

Are we to conclude that nitrification occurs in all depths of the subsoil at which the nitrifying agent exists? I am strongly of

* In taking the averages, soils 6 and 12 inches deep have been reckoned as 9 inches; soils 18 inches as 16 inches; and 27 inches as 2 feet.

opinion that nitrification is practically confined to the surface soil, and occurs rarely, and to a very small extent, in a clay subsoil removed 2 or 3 feet from the surface. All the conditions for nitrification are present to a far greater extent in the surface soil than in the subsoil. The surface soil is in the large majority of cases far richer in nitrogenous matter suitable for nitrification than the subsoil. At the surface also, the amount of oxygen available is immeasurably greater than it is below. The principal hindrance to nitrification in a clay subsoil is in fact the impossibility of obtaining a sufficient circulation of air at considerable depths.

The amounts of nitric acid annually produced by the three masses of soil forming the drain gauges at Rothamsted are not in favour of any important portion of this product being generated in the subsoil. These masses of soil were originally portions of an arable field; they were isolated without being disturbed. They are of the same area, but of different depths. The quantity of nitric nitrogen annually found in the drainage waters from these soils has, on an average of nine years, been as follows:—

Soil 20 inches deep, 40·2 lbs. per acre.
„ 40 „ 35·0 „ „
„ 60 „ 38·8 „ „

There is here no evidence of any greater production of nitrates where the subsoil is included in the experiment.

The evidence obtained by analysing fallow soils at different depths points to the same conclusion. If after a cereal crop, which has removed the nitrates from the soil, the land be cultivated during the next summer as a bare fallow, the nitrates formed during this season of rest and tillage will be found chiefly in the surface soil, unless heavy rain has occurred to wash them below. Thus a fallow soil in Agdell Field at Rothamsted, sampled on September 8, 1882, yielded the following quantities of nitrogen as nitrates:—

First 9 inches, 40·1 lbs. per acre.
Second 9 inches, 14·3 lbs. per acre.
Third 9 inches, 5·5 lbs. per acre.

There can be no doubt that a considerable part of the small quantity of nitrates found in the subsoil had not been formed *in situ*, but had been carried to this depth by drainage and diffusion.

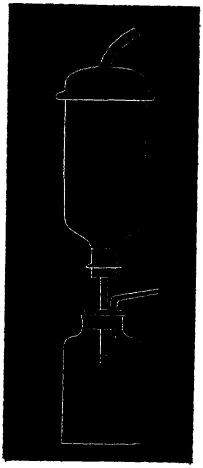
The discovery of large quantities of nitrates in a subsoil is no proof that they have been produced there; their occurrence at this depth is a natural result of drainage and diffusion in the absence of a growing crop capable of removing them from the soil. An accumulation of nitrates in the subsoil below the ordinary depth to which the roots of crops extend is quite possible, and such accumulations may remain little altered in quantity from year to year, the annual additions balancing the annual waste by drainage.

The conditions which favour nitrification in the subsoil are such as enable air to penetrate it. Artificial drainage; a dry season; or the growth of a luxuriant crop, causing much evaporation of the water of the soil: such conditions, by removing the water that fills the pores of the subsoil, will cause air to penetrate more or less deeply, and render nitrification possible. A small amount of subsoil nitrification may thus take place in the drier periods of the year.

The nitrogenous matter existing in a clay subsoil is not only small in quantity, but also different in composition from that found in the surface soil. At Rothamsted, the ratio of nitrogen to carbon in the surface soil of the arable fields is about 1 : 10, while at 54 inches from the surface the proportion is only 1 : 6. The nitrogenous matter existing in the subsoil is apparently susceptible of nitrification, if placed under perfectly suitable conditions.

Experiments on the nitrifiability of soils and subsoils from Manitoba have been already published by Messrs. Lawes and Gilbert (Trans., 1885, 410). The subsoils, freely exposed to air in a covered basin, were found to yield nitric acid, especially during the last period of the examination, when they had been supplied with nitrifying organisms from a fresh surface soil.

Some trials of the nitrifiability of clay subsoils were made in 1884. The surface soil (1st 9 inches), and a subsoil (3rd 9 inches) from two arable fields at Rothamsted were the subject of experiment. 100 grams



of dry powdered soil were mixed in each case with the same weight of coarsely powdered recently ignited flint, and the mixture placed in cylindrical funnels, consisting of narrow-necked pint bottles having their bottoms removed. Each funnel was connected by a cork and tube with a bottle, into which any liquid draining from the funnel could pass. The funnel was closed at top by a tubulated caoutchouc cap. The tubulure contained cotton-wool moistened with weak sulphuric acid. The bottle receiving the drain water was also closed with a cork, and provided with a tubulure containing acidified cotton-wool. The passage of air through the apparatus was thus permitted, but any ammonia the air might contain was removed before entrance. As all the soils had been dried (at a temperature of about 56°), and any nitrifying organism they contained probably killed, they were each seeded by mixing with them 0·10 gram of fresh surface soil. In each case, the subsoil was experimented on in duplicate, one lot receiving 0·5 gram potassium phosphate, 0·5 gram magnesium sulphate, and 5·0 grams of calcium carbonate, and the other lot being without this addition.

The soil mixtures when placed in the funnels were treated with successive quantities of ammonia-free water till all ready formed nitrates were removed; the soils were then placed in the dark to nitrify. From time to time, the soils were extracted with ammonia-free water to remove the nitrates which had been produced; the extraction was performed without removing the soil from the funnel. The quantities of nitrates found in the successive watery extracts are shown in the following tables:—

Nitric Nitrogen obtained from 100 *grams of Soil and Subsoil from Plot* 10A, *Broadbalk Wheat Field.*

	Surface soil (1st 9 inches).	Subsoil (3rd 9 inches).	
		Alone.	With cinereal plant food.
	gram.	gram.	gram.
Jan. 24th—Feb. 9th (16 days)......	0·00067	trace	trace
Feb. 9th—Mar. 1st (21 days)	0·00093	0·00002	0·00022
Mar. 1st—Mar. 28th (27 days)	0·00053	0·00004	0·00061
Mar. 28th—May 9th (42 days)	0·00037	0·00050	0·00027
May 9th—Dec. 12th (217 days)	0·00135	0·00073	0·00104
Total nitric nitrogen obtained......	0·00385	0·00129	0·00214
Nitric nitrogen per 100 of original nitrogen	3·8	2·4	4·0

Nitric Nitrogen obtained from 100 grams of Soil and Subsoil from Plot O2, Hoos Barley Field.

	Surface soil (1st 9 inches).	Subsoil (3rd 9 inches).	
		Alone.	With cinereal plant food.
	gram.	gram.	gram.
Mar. 18th—April 17th (30 days) ...	0 00023	0·00004	0·00015
April 17th—May 20th (33 days) ...	0·00060	0·00062	0·00064
May 20th—Dec. 23rd (216 days) ...	0 00086	0·00052	0·00063
Total nitric nitrogen obtained......	0·00169	0·00118	0·00142
Nitric nitrogen per 100 of original nitrogen	1 9	3·0	3·6

The amounts of nitrate obtained from the experimental soils and subsoils at different periods are far from regular; we need not here, however, discuss the causes of this irregularity, our object being simply to show that the nitrogenous matter of a clay subsoil is nitrifiable, and of this fact the figures leave no doubt. The quantity of nitrates produced in the subsoil is smaller in every case than in the surface soils, but the proportion of the original nitrogen of the soil which was nitrified is on the whole quite as large in the case of the subsoils as in that of the surface soils.

XVIII.—*The Influence of Silicon on the Properties of Iron and Steel.*
Part I.

By Thomas Turner, Assoc. R.S.M., Lecturer on Metallurgy, Mason College, Birmingham.

Introduction.

It is now about 30 years since the researches of Deville so largely extended our knowledge of the properties of silicon, and trustworthy analyses of iron and steel, including estimations of silicon, date from about the same period. It is true that in exceptional cases accurate analyses had been performed before this, but the wider extension of trustworthy work is closely connected with the school of chemists trained by Dr. Percy at the Royal School of Mines, and including such men as Dick, E. Riley, R. Smith, Snelus, J. Spiller, and Willis. Since this period, a vast multitude of analyses have been performed, and so many facts observed, that one is quite overcome with the amount of material, and the difficulty of extracting anything definite and certain from among so much that appears contradictory.

It would be undesirable at this point to attempt more than a brief outline of the history of the subject of silicon in iron and steel, though a short reference to the matter appears necessary.

In 1870 Snelus (*Jour. Iron and Steel Inst.*, i, 34, 38) published an analysis of a steel containing 0·64 per cent. of silicon, the other elements present being in about the usual quantity (C. 0·55, S. 0·07, P. 0·04, Mn. 0·55). This metal was brittle, and its brittleness Snelus attributed to the presence of silicon, remarking, "When present in Bessemer steel to the extent of one-tenth per cent., silicon has the effect of rendering the metal hard and brittle when cold." On the same occasion, in discussing the paper of Snelus, Sir H. Bessemer stated that a certain small proportion of silicon was necessary for the production of good crucible steel. This opinion was more fully expressed later, and what appeared to be absolute proof of the correctness of Sir H. Bessemer's views was published in 1877 (*ibid.*, 1877, i, 82). The value of silicon for imparting soundness to crucible steel was also mentioned by H. Bell (*Chem. News*, **40**, 102); much silicon was said to produce both red and cold shortness, and under certain conditions to impart hardness. Dr. Percy (*Iron and Steel*, p. 847) had mentioned a number of years earlier, that the late Mr. S. H. Henry entertained the opinion that silicon was essential to good steel, and was as important as carbon. On the other hand, as supporting Snelus, it is believed that silicon renders malleable iron hard and brittle, and that it has the same effect on steel rails, so that it has been specified for soft rails that the silicon should not exceed 0·04 per cent., though a somewhat higher limit is generally adopted. In 1872, a lecture was delivered before the Chemical Society by E. Riley, "On the Manufacture of Iron and Steel" (*Jour. Chem. Soc.*, 1872, **25**, 536), in which an account was given of the preparation of a silicide of iron containing nearly 22 per cent. of silicon, and made by heating a mixture of ferric oxide, sand, and charcoal in a Siemens furnace. A tool was prepared by melting together sheer steel, siliceous iron, and spiegeleisen, the product containing 2·07 per cent. of silicon, the other constituents not being given. The metal was tough, worked well under the hammer, and appeared to be excellent steel. Mr. Riley also mentioned a specimen of so-called titanium steel, which was of excellent quality, though it contained 1·32 per cent. of silicon and no titanium. It was concluded that these silicon steels were as strong as ordinary crucible steel, and were not deteriorated by the silicon present. Mr. Riley also suggested the use of siliceous iron in steel making, for the production of sound castings, an application which has since been largely adopted. An intention was expressed to conduct experiments on the effect of the addition of siliceous iron on the strength of steel castings, but unfortunately Mr. Riley was unable to carry out his intention.

In 1872, Mrázek published the results of some very interesting experiments on the effects of silicon and manganese on the properties of steel (*Berg und Huttemänm. Jahrbuch*, 1872, **20**, 406—519; Gautier, *Bull. Soc. Ind. Minérale* [2], **4**, 383; *Inst. C. E.*, **44**, 316). In these experiments silicide of iron was prepared containing only a trace of carbon and 7·42 per cent. of silicon. It welded perfectly; forged well at a red or at a white heat; it was magnetic, brittle at ordinary temperatures, hardness 5 to 6, and hardened slightly when quenched in water from a red heat.

Mräzek concluded that silicon and carbon are detrimental to the malleability at a red heat, whilst manganese is advantageous. Carbon is more detrimental than silicon, especially at a high heat, whilst a white heat renders the favourable effect of manganese more sensible. In these experiments, however, comparatively small quantities of metal were used, and the power of welding and forging was principally considered.

Writing on the manufacture of steel in 1875, W. Hackney (*Inst. C. E.*, **42**, 35) stated that silicon produces hardness in steel, and that "it is probable that the hardness produced by silicon is coupled with more brittleness, that is, with less extensibility, particularly under a suddenly applied strain, than is due to carbon, and its presence in a proportion exceeding 0·1 to 0·2 per cent. in steel for rails is looked on as unsafe." Even this quantity was regarded as apt to be unsafe, but it was considered that with tool steel, if otherwise of good quality, 2 per cent. of silicon may not be injurious.

In 1878 R. Åkerman published some important remarks in a paper on "The Most Recent Advances in the Manufacture of Iron and Steel as Illustrated by the Paris Exhibition" (*Jour. Iron and Steel Inst.*, 1878, ii, 359). In considering the use of silicon for the production of sound castings at Terre Noire, it was stated that silicon promotes the compactness of the metal, but does not otherwise improve its qualities. The addition of silicon is a necessary evil, but any excess should be avoided, as rendering the metal more sensitive to blows. For ingot iron, to be shingled or rolled, M. Pourcel would on no account allow of any addition of silicon. For steel castings, 0·2 to 0·3 per cent. was recommended, and considered to be tolerably harmless. Åkerman also considered it well established that manganese counteracts the injurious influence of silicon.

G. J. Snelus,* writing about 1879, said, "Silicon produces both red shortness and cold shortness in steel. In the absence of carbon these effects are not very marked, but when small proportions of carbon are present the action of silicon is very decided. Thus when carbon is under 0·1 per cent., silicon may exist up to 0·6 per cent. or more without rendering the steel particularly brittle. Such steel could be heated and quenched in water, and afterwards bent double without cracking, while the tensile strength was not greatly increased. It also worked well at a bright red heat. On the other hand, when carbon rises to 0·4 or 0·5 per cent., even 0·2 per cent. silicon produces decided red shortness and cold shortness, and if the silicon reaches ½ per cent., these qualities are developed to a dangerous extent." Snelus refers also to the advantage of silicon for steel castings, and gave the following analysis of a silicon steel:—

Carbon	0·40
Silicon	2·44
Sulphur................	0·06
Phosphorus	0·03
Manganese	0·88

This metal had a tensile strength of 48 tons, and an elongation of only 3 per cent.

Writing in 1882, Snelus made further observations on the same subject (*Jour. Iron and Steel Inst.*, 1882, ii, 582), with special reference to rail steel. From the average composition of 32 slow-wearing rails, Dr. Dudley had deduced the following ideal composition for good wearing rails:—

Carbon	0·334
Silicon	0·060
Phosphorus	0·077
Manganese	0·491

Snelus suggested that for British rails the silicon might with advantage be raised to 0·1 or even 0·15 per cent., whereby the steel would be improved without being seriously hardened; while a steel containing less carbon and more silicon would fail under the bending and concussive tests.

In 1882, M. Pourcel (*ibid.*, 1882, ii, 513, 517, 532), of Terre Noire, recommended from 0·15 to 0·2 per cent. of silicon in steel for the hoops of guns, and stated that "metal made with silicide of iron always remains brittle under the drop test, and gives but low extension under tensile strain, with a low and variable breaking load. These bad qualities come to light in forging. The metal cracks under the blows of the hammer, whilst metal made with silicide of manganese behaves in a much more satisfactory manner."

---

* Article "Steel," *Chemistry Applied to Arts and Manufactures*, p. 878.

Pourcel considered silicon to be the *indirect* cause of the bad qualities observed during forging, and especially in rolling. The compact homogeneous character of the ingot, and its freedom from blowholes, prevented its adapting itself so readily to the rough work of rolling as in the case of a spongy ingot. Hence "silicon should be avoided not so much as a hardening element, but on account of the homogeneity it gave to the metal."

Lastly, to close this imperfect summary of what has already been published on the subject, we are indebted to M. F. Gautier for much information. His translation of Mräzek's important paper into French has already been quoted, while M. Gautier's paper on "Solid Steel Castings" (*ibid.*, 1878, i, 40) did much in directing the attention of steel makers in England to the value of silicon, when properly employed, for steel foundry purposes. M. Gautier has since expressed the opinion that for tool steel, with 0·2 per cent. of carbon, 1 per cent. of silicon might be present without injury (*ibid.*, 1884, ii, 399); and in a recent letter draws my attention to the "Vickers (Sheffield) special steel for tyres, which contains 1 per cent. of silicon, and which was for its qualities a great novelty in France two or three years ago. The French manufacturers, however, can now make this easily, as they have discovered that this superiority is due to silicon."

Some of the statements I have quoted are doubtless contradictory, and are not capable of being reconciled; but in many instances what at first sight appears to be contradictory can be shown to be harmonious on account of the great difference in the properties of the commercial varieties of iron and steel. Dr. Percy stated many years ago that different varieties of iron met with in the arts differed from each other more than did some actually distinct metals; and practically ingot iron, moderately hard steel, and crucible steel differ so much in properties that it is necessary to consider them separately when the effect exerted by any foreign element is examined. Probably the present state of our knowledge may be briefly summarised as follows:—

1. *Ingot Iron.*—Silicon promotes soundness; it resembles carbon in increasing the tenacity and hardness; it should not exceed 0·15 per cent. if the metal has to be rolled; and in some cases it produces brittleness when cold.

2. *In Steel Castings.*—Silicon promotes soundness; it is, however, regarded as a necessary evil, and excess should be avoided as tending to brittleness and low extension; about 0·3 per cent. is generally recommended.

3. *In Crucible Steel.*—A few hundredths per cent. is necessary to

produce soundness; and it is generally agreed that considerable quantities of silicon may be present without injury.

4. Manganese appears to be capable of neutralising the ill effect due to silicon. The effect of carbon is somewhat doubtful; Mrázek's experiments appear to show that the presence of carbon is detrimental to silicon steel.

Silicon in Specially Pure Iron.

My experiments were commenced in 1883, the original intention being to add pure silicide of iron to pure iron in different proportions, and to examine the product (Trans., 1884, **45**, 260; 1885, **47**, 474). During the first two years, all my efforts in this direction ended in failure, partly owing to the difficulty of preparing a pure silicide in considerable quantities, also to the insufficiency of any laboratory apparatus for the treatment of the necessary amounts of material with so high a melting point; and, lastly, when a Siemens furnace was used, much trouble was experienced in obtaining a suitable crucible capable, on the one hand, of resisting the high temperature, and yet which should not impart silicon, carbon, or other substances to the metal employed. In consequence of these failures, my attention was directed to the subject of silicon in cast iron, as the lower melting point of cast iron allowed of its manipulation with the apparatus at my disposal. These results have already been brought before the Society (Trans., 1885, **47**, 577, 902; 1886, **49**, 130, 215, 493; *Jour. Soc. Chem. Ind.*, May, 1886; *Jour. Iron and Steel Inst.*, Part I, 1886, p. 163), and the facts then published have been applied in England for the production of many thousands of tons of castings, the quality being better and the price lower than was obtained with similar material before. The method has also been successfully applied in Scotland, and by upwards of 100 founders in France,* besides being used elsewhere on the Continent and in America. The experiments now to be described are, however, chiefly of theoretical interest, and there is no reason to anticipate any such practical application.

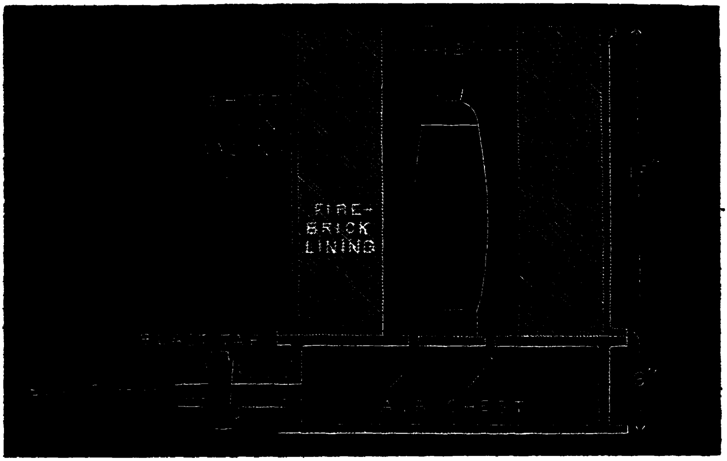
Finding it impracticable to conduct these experiments in the laboratory, I applied to Mr. Percy Gilchrist for an opportunity to conduct them at a basic steel works, as the low percentage of silicon usually present in basic steel apparently rendered it a very suitable material for the purpose. By the kindness of Mr. Gilchrist I was introduced to Mr. Hutchinson, manager of the South Staffordshire Steel and Ingot Iron Co., Bilston, who afforded me every opportunity for experiment, and to whom I am indebted for the kindly interest manifested in the work.

---

* Gautier, "Silicon in Foundry Iron," *Jour. Iron and Steel Inst.*, Part II, 1886; *J. Soc. Chem. Ind.*, 1886, p. 606.

For the purpose of these experiments a small furnace was erected on the platform between two Bessemer vessels. A sketch of this is given in Fig. 1, from which it will be seen to be a slightly modified Deville furnace, capable of containing the crucible used. The blast was supplied by means of a pipe from the blast main of the works, while coke was used as fuel.

FIG. 1.



The crucibles used were of Stourbridge fire-clay, and were capable of holding about 35 lbs. of steel. After the necessary annealing, the pot was placed in the furnace and raised to about the melting point of cast iron. A few minutes before the mixture was to be made, a weighed quantity of silicon pig was introduced into the crucible, and the temperature increased by turning on more blast. At the right moment, the crucible was rapidly removed from the furnace and brought near to the mouth of the converter, while at the same time the men drew a ladle of metal from the vessel. This was poured into the crucible, and the metal well stirred by means of a rod of basic steel. The mixture was allowed to cool in the crucible, which was afterwards broken, the ingot so obtained being immediately numbered and afterwards examined.

The metal was taken from the converter at the end of the blow just before the addition of ferromanganese, and was therefore a very near approach to chemically pure iron. Its composition was found to be—

Carbon	0·02	per cent.
Silicon	0·0098	,,
Sulphur	0·039	,,
Manganese	0·06	,,
Phosphorus	0·04	,,

This metal was difficult to obtain in a sound ingot, and several attempts were made before this was accomplished. In the first experiment, 30 lbs. was poured into the pot, and remained perfectly quiet in the crucible for a few moments, but on solidifying it suddenly boiled up, and although the crucible was not full originally, 22½ lbs. boiled over the edge of the vessel, while only 7½ lbs. remained in the pot. No such action was observed in any mixture to which silicon had been added, and an addition of only 0·04 per cent. of silicon (of which only 0·02 afterwards remained in the ingot) was sufficient to prevent this boiling over on solidification.

This action, though striking when first observed, is not new, since M. Pourcel has stated that his experience at Terre Noire had shown that a few hundredths per cent. even of silicon was capable of causing the metal to lie quietly in the moulds. But the first observation of the fact is probably due to Sir H. Bessemer, who announced as early as 1861 that a minute quantity of silicon prevented steel ingots from becoming porous or cellular, and patented in the same year the addition of 1 lb. of silicium to 2000 lbs. of molten steel, to prevent this tendency to ebullition, and cause the metal to lie quietly in the mould (Jeans, "Steel," p. 604).

In making these mixtures, it was considered doubtful at the time, in three cases, whether thorough incorporation had taken place. These ingots will be referred to as "doubtful mixtures," and in one case at least the doubt was afterwards found to be justified. To the numbers of these ingots, the letter D is attached.

The siliceous iron employed had the following composition:—

Carbon	1·96	per cent.
Silicon	10·30	,,
Sulphur	0·02	,,
Manganese	1·90	,,
Phosphorus	0·17	,,

This probably represents the most suitable material obtainable in considerable quantities which could be found for such experiments. The use of pure silicide prepared by the action of sodium has been suggested. To this there are several objections, one of them being the difficulty of obtaining a large quantity of such material with a uniform composition. Further it has been shown (*Watts's Dict.*, **3**,

370) that iron is capable of combining with considerable quantities of potassium when strongly heated with it, and it is highly probable that silicide of iron prepared in the manner suggested is not so pure as has been supposed. In using a silicon pig with a composition as above we employ a material actually available if necessary for use on the large scale, and the only impurities present in any quantity are carbon and manganese, neither of which amount to one-fifth of the silicon present, and both of which are always present in even the purest commercial varieties of iron. Further, the influence of carbon and manganese on iron has been long studied, and is pretty accurately determined, whilst that of the alkali metals is at present obscure.

Rolling Tests.—The ingots obtained in the manner described were reheated and rolled by workmen experienced in the manipulation of basic and other mild steel. The results are given below, and from these it will be seen that some ingots were successfully rolled into the desired round bar of 1⅜ inch diameter, while others were not able to bear this treatment.

1. Ingots which could be rolled.

No.	Si added.	Si found.	Remarks.
1	0·0	0·0098	Cracked at first, but closed up, and a rather spongy bar was obtained.
2	0·04	0·02	Cracked badly, but afterwards closed up, and gave a fair bar.
D 3	—	0·027	Ditto.
4	0·10	0·035	Ditto.
5	0·07	0·039	Ditto.
6	0·13	0·08	Ditto.
7	0·22	0·117	Rolled rather better than previous ones.
D 8	0·23	0·13	Like No. 6.

2. Ingots which could not be rolled.

No.	Si added.	Si found.	Remarks.
9	0·18	—	Rolled to 4″, then nearly cracked to pieces.
D 10	0·21	—	Very red short, dropped to pieces at 2″ bar.
11	0·23	—	Cracked very badly, only able to get to 2″.
12	0·30	0·27	Very red short, broke in pieces at 4″.
13	0·50	0·40	Went to pieces under the steam hammer.

The letter D signifies that thorough mixture was rather doubtful.

A glance at these results shows that silicon renders the metal red short, and is detrimental to successful rolling. The original metal, owing to the absence of manganese, was somewhat red short, but this character was not very noticeable in the rolling tests, nor did it become so with the mixtures to which less than 0·15 per cent. of silicon had been added, or in which less than 0·1 per cent. remained in the ingot. With a few hundredths per cent. over this amount, however, the results were irregular, and when a little more silicon was present the ingots uniformly went to pieces. It will be seen that the amount of silicon found by analysis is always less than that calculated, but the difference is not very regular. This irregularity is due partly to errors in weight of the ingot, which could not be made always of the same weight, and which was afterwards only roughly weighed to a quarter of a pound on a pair of scales. A more important cause of irregularity would be the difference in the amount of dissolved oxidising gases in the metal. It is possible also that the silicate produced by these gases may be of varying composition, depending on the amount of silicon present.

Doubtless the amount of silicon necessary to produce red shortness would be increased if more manganese were present. But these results appear to quite confirm the general impression among steel makers, that for metal which has to be rolled the silicon should not exceed 0·15 per cent.

Chemical Analysis.

It will be well perhaps at this point to give the chemical analysis of those ingots which were capable of being rolled, and which were further examined. It was not considered necessary to examine the fragments of the ingots which fell to pieces in the rolls, as the other metal was found to be very uniform in composition, and only differed from the very red short material by containing less silicon.

No.	C.	Si.	S.	Mn.	P.
1	0·02	0·0098	0·039	0·06	0·04
2	0·029	0·02	0·03	0·10	0·03
D 3	0·02	0·027	0·028	0·07	0·042
4	0·076	0·035	0·03	0·10	0·06
5	0·057	0·039	0·03	0·09	0·05
6	0·052	0·08	0·036	0·09	0·06
7	0·113	0·117	0·015	0·08	0·045
D 8	0·034	0·13	0·033	0·09	0·08

The chemical analyses were performed by my friend Mr. J. P.

Walton, of the Glasgow Iron Co., Wishaw, who has very considerable experience in the analysis of basic steel, and to whom I am indebted for valuable assistance on former occasions.

In several instances, where the results were somewat unexpected, I have checked them by independent analyses, but in each case have only confirmed Mr. Walton's results.

The combined carbon determinations are my own, the method employed being the Eggertz coloration test as modified by Stead for small quantities of carbon. The standard employed contained 0·10 per cent. of carbon, as estimated by combustion, and was itself a mild basic steel. It will be seen that the carbon varies, not very regularly, from 0·02 to 0·113 per cent. This will of course somewhat modify the results, though I do not believe the influence is very marked; it is of course very difficult to avoid slight variations when dealing with quantities which are only measured in hundredths per cent. The sulphur only varies between 0·015 and 0·039 per cent., the manganese between 0·06 and 0·10 per cent, and the phosphorus from 0·03 to 0·06 per cent, so that the metal was as uniform in composition as could reasonably be anticipated.

Hot Tests.—In these tests, it was considered advisable to follow as closely as possible those methods which are actually employed by manufacturers. Owing to my own inexperience in this class of tests, and the necessity of performing them at the works, this part was superintended by my friend Mr. F. W. Harbord, chemist to the South Staffordshire Ingot Iron Co., Bilston, at whose works these experiments were conducted. It is with much pleasure that I acknowledge the help I have received from Mr. Harbord, and his extensive experience in this class of tests renders the work of much more practical value than it otherwise could have been.

In the hot tests, the 1$\frac{3}{8}$-inch bar was strongly heated, and then plated out under the hammer, so as to form a flattened surface with thin edges. Metal free from red shortness should stand such treatment without cracking at the edges, and in case of a more severe test should be bent over once or twice without showing any crack at the bend. In the bars examined, however, in every case distinct signs of red shortness were visible on plating out, the edges becoming cracked, and in a few cases pieces of metal actually broke off during the test. The report on the metal without addition of silicon was as follows:—"One end of bar was plated out; it was very red short, and cracked badly on edges. Worked very well at a bright red heat, but was red short at a dull red heat." In the other cases, the reports were so similar that it will be unnecessary to quote them; the specimens certainly did not improve with the addition of silicon, but, if anything, became worse. It must be borne in mind also that in these tests only that metal which could be rolled was examined, and hence the ingots which were particularly red short had already been eliminated.

Cold Tests.—The cold test adopted consisted in bending the 1⅜-inch bar parallel with itself, that is, through 180°, with a radius which never exceeded half an inch. This is considered a fairly severe test for cold shortness. In these tests also the results were remarkably uniform, though unexpected. They are as follow:—

No.	Si per cent. found.	Remarks.
1	0·0098	Bent without fracture; in places the bar opened slightly, but this was due to cracks during rolling.
2	0·02	Very good; bent over parallel without fracture.
3	0·024	Do. do.
4	0·035	Do. do.
5	0·039	Do. do.
6	0·08	Do. do.
7	0·117	Do. do.
8	0·13	Bent over close without slightest crack.

It will be seen, therefore, that the specimens were all very tough, and stood the cold test remarkably well. I shall mention later a tool made with metal higher in silicon: this also was remarkably tough. I believe, therefore, that the brittleness which has been attributed to the presence of silicon in mild steel is either due to some other cause or to a secondary effect produced in the presence of some other constituent.

Welding Tests.—These tests were performed on pieces of the same 1⅜-inch round bars mentioned previously. The whole of the tests were made by the same workman, and perfectly clean surfaces of the metal were used, no sand, borax, or any other material being added. The results are as follow:—

No.	Si per cent.	Remarks.
1	0·0098	Bar welded well; in breaking through the weld no trace of line of junction visible. Worked well at bright red heat; red short at dull red heat.
2	0·02	Broke in two during welding, owing to red shortness.
D 3	0·024	Weld very good; worked well at welding heat, but red short at low red heat.
4	0·035	Do. do.
5	0·039	Do. do.
6	0·08	Do. do.
7	0·117	Do. do.
D 8	0·13	Weld not so good; otherwise the same.

It will be seen therefore that the specimens welded uniformly well, with the possible exception of No. 8, which was not so good. The red shortness of the material naturally interfered to some extent, as the metal had to be kept pretty nearly at a welding heat while working. In perfection of weld, however, no perceptible difference resulted from the addition of silicon, as the metal with only 0·0098 per cent. welded perfectly.

Considerable difference of opinion has been expressed on this subject by various writers, some having considered silicon necessary for the production of a good weld, whilst Hupfield has stated that silicon diminishes the welding properties of the metal to such a degree, that steel with 0·45 to 0·5 per cent. of silicon is welded with difficulty, and with 0·5 per cent. it cannot be welded at all. A commission was appointed in 1880 by the German Society for Promoting Technical Industry to inquire into the capacity of different irons for welding. E. P. Boehme, in giving an account of the conclusions arrived at (*Dingl. polyt. J.*, **251**, 71—77; Abstr., 1884, 786), states that in bar iron silicon increases, whilst manganese decreases the power of welding. This is due to the fact that during the oxidation in welding, silicon produces a slag by dissolving the oxide formed, and so producing a clean surface. In ingot iron, however, the amount of silicon is the same before and after welding, and the welding property appears to be uninfluenced by the proportion of silicon. And, as has been previously mentioned, Mräzek prepared a silicide of iron, containing 7·42 per cent. of silicon and only a trace of carbon, which welded perfectly. These facts, taken with my own results, show that in mild steel or ingot iron the property of welding is but little affected by the amount of silicon present, since iron will weld perfectly with silicon varying from 0·0098 to 7·42 per cent.

Mechanical Tests.—The experiments hitherto mentioned as connected with the working properties of the metal were all performed at the works, and are of a qualitative character. We have now to deal with mechanical tests as adopted by engineers. These were performed by Professor A. B. W. Kennedy in the engineering laboratory of University College. I have on previous occasions acknowledged my indebtedness to Professor Kennedy, whilst the interest he has taken in these experiments, and the important part he has performed in them, very much increases this obligation.

For the purpose of these experiments, turned test pieces were obtained, under my own superintendence, from each of the ingots which were rolled into bars. The turnings obtained at the same time were preserved for analysis. These test pieces were round bars, rather over 16 inches in total length, and with $1\frac{1}{4}$ inch diameter Whitworth screws in each end to fit the testing machine. The portion to be tested was about 12 inches long and 1 inch in diameter. The pieces were finished at University College, accurate measurements being taken, and a length of 10 inches being used in the measurements of extension. In each case duplicate experiments were performed, and the results so obtained were generally quite as concordant as could be anticipated. I have thought it well to give the whole of the actual results in Table A (p. 146), as an appendix to this paper, but for convenience have selected the more important results in a separate table, B, the values in each case being the mean of two experiments. For comparison I have added my own determinations of relative hardness, to which subsequent reference will be made.

TABLE B.—*Mean Results of Tensile Tests.* Professor KENNEDY.

No.	Si. p. c. found.	Limit of elasticity. Tons per sq. in.	Breaking load. Tons per sq. in.	Ratio limit to break.	Extension per cent. on 10 inches.	Reduction of area per cent.	Relative hardness.
1	0·0098	13·01	21·80	0·597	27·7	77·0	18
2	0·02	13·08	19·95	0·656	17·6	40·3	16
D 3	0 027	17·75	21·75	0·861	26·0	67·4	15
4	0·035	15·69	23·07	0·680	16·3	31·8	17
5	0·039	16·42	23·28	0·704	18·2	37·7	17
6	0·08	16·72	23·77	0·704	24·2	44·9	20
7	0·117	18·00	28·05	0·642	15·6	26·8	21
D 8	0·13	18·37	25·68	0·715	18·8	41·9	20

An examination of Table B shows that the influence of silicon is tolerably uniform and well marked. The most notable exception to this is in the case of No. 3, which in breaking load, extension, and reduction of area very closely resembles the metal to which no silicon was added, though, on the other hand, its elastic limit is rather higher than might be anticipated. This specimen is, however, very exceptional. It will be noticed in Table A that Professor Kennedy mentions the fact that this specimen actually gave out a cloud of siliceous dust when broken, and that in appearance the fracture of the bar was very peculiar. Three large and about 20 small round pipes or hollow tubes, which were probably due to imperfect welding during rolling, could be seen in the specimen, these being partly filled with siliceous matter in the form of a nearly white powder. Of this iron, I have brought a fractured test piece, in order that its remarkable appearance may be examined. I shall, however, not further consider the matter now, as Professor Kennedy intends to refer to this, in connection with other observations of a similar kind, at some future time, and I have also myself made some as yet unpublished experiments in connection with the occurrence of silica in certain cases.

It may be mentioned, however, that on dissolving this specimen in an acid, for estimating the silicon, white flakes of silica are obtained, which are different in appearance from the gelatinous silica generally produced. It is probable, therefore, from the appearance of the fracture, the values obtained in the mechanical tests, and the peculiar way in which silica separates on solution, that the silicon in this specimen is present in the *oxidised* condition. A similar observation was also made in No. 8, though in this case the silica was not so noticeable; but it may be pointed out that both the ingots in which silica was observed were imperfect mixtures, and this appears to be in some way connected with the result. It may be explained further that in making these mixtures the silicon pig was not quite as hot as usual, and so was not melted before pouring in the molten steel; and though the mixture was well stirred, it was considered doubtful whether the whole of the silicon added was intimately mixed with the metal.

We will now examine the results more in detail.

Modulus of Elasticity.—An examination of Table A (p. 146) shows that the specific extension under a tensile stress (ϵ_t), or under a compressive stress (ϵ_c), is tolerably uniform throughout the series of specimens, and no influence in this respect can be traced to the presence of silicon. As the extension is uniform, we naturally find the modulus of elasticity tolerably regular also, and about the usual value for such material. The modulus of elasticity, therefore, does not appear to be sensibly affected by the small amount of silicon added in these experiments.

Limit of Elasticity.—On referring to Table B (p. 142), it is seen that the limit of elasticity gradually increases as the proportion of silicon becomes greater, rising from 13·01 tons with 0·0098 per cent. of silicon, to 18·37 tons with 0·13 per cent. No. 3 is the only exception to this regular increase, and has been already mentioned. In this connection, however, it must be noticed that the carbon also varied 0·09 per cent. in this series, and though by no means regular, still it tended to increase with the silicon. Carbon is known to increase the elastic limit, and silicon is believed to act in a similar manner. These results appear to give considerable support to this belief. For mild steel of 28 to 30 tons an elastic limit of at least 17 to 18 tons per square inch may fairly be expected, and only three of the specimens examined gave so high a value.

Tensile Strength.—The breaking load with 0·0098 per cent. of silicon was 21·8 tons; this shows a tendency to increase with more silicon, reaching a maximum of 28·05 tons with 0·117 per cent. In three cases, the results, though in ascending order if considered together, are lower than might be anticipated from the remaining values.

In two of these, Nos. 3 and 8, the silicon was partly in the *oxidised* condition, as before mentioned, which fully accounts for the difference; in No. 2, however, the cause of the slightly reduced tensile strength is doubtful. Mild basic steel generally has a tensile strength of about 27 tons; this is not exceeded in any of these samples, and only reached in one instance.

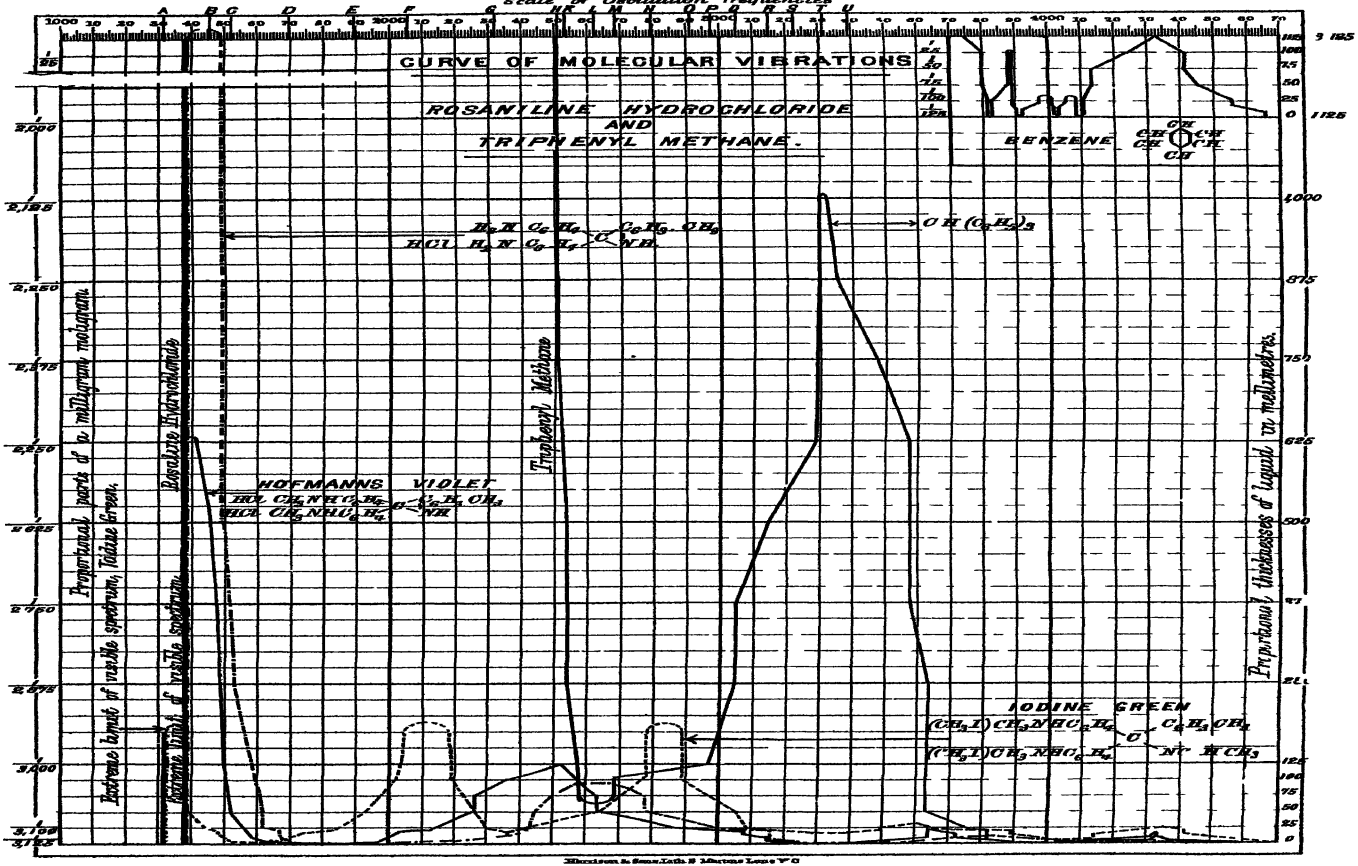
The ratio of limit to break is not very regular, but appears to increase on the addition of silicon, which is the converse of what happens on an increase of carbon.

Extension.—The extension per cent. on 10 inches in the original metal was 27·7 per cent., while in No. 3, with oxidised silicon, the extension was 26 per cent., both of which are rather unusually high values. No. 6 is the only other specimen with a high value (24·2 per cent), and is exceptional, all the others being low in this respect, reaching a minimum of 15·6 per cent., while 20 per cent. is stipulated with mild steel. It appears, therefore, that a few hundredths per cent. of silicon is capable of very much reducing the extension, and would on that account be detrimental.

Reduction of Area.—The reduction of area per cent., which is a measure of ductility, naturally follows the extension pretty closely. It is a property which is very much affected by flaws or irregularity in the character of the material. In this class of mild steel, the reduction of area should be at least 50 per cent., while values up to 70 per cent. are sometimes obtained. The original metal with 77 per cent. reduction was therefore exceptionally good, but fell to 40·3 per cent. with 0·02 per cent. of silicon, and 31·8 per cent. with 0·035 of silicon. In the other bars, the extension was low in each case, and was also irregular.

Appearance of Fracture.—On referring to Professor Kennedy's remarks, as given in Table A, it will be seen that the addition of silicon produced a marked change in the appearance of fracture. In the absence of silicon, the bar was finely silky in fracture; and it was also silky in the presence of *oxidised* silicon, as in No. 3. The presence of silicon, however, when in combination with the iron, rendered the fracture more or less crystalline, and often irregular. Some allowance must be made, of course, for the red shortness of the material, which would interfere with the parts uniting perfectly during rolling. Judging from the appearance of the specimens fractured by a tensile force, the quality of the metal was not improved, but otherwise, by the presence of silicon. It may be mentioned that if nicked with a chisel and broken across, the metal appeared uniform

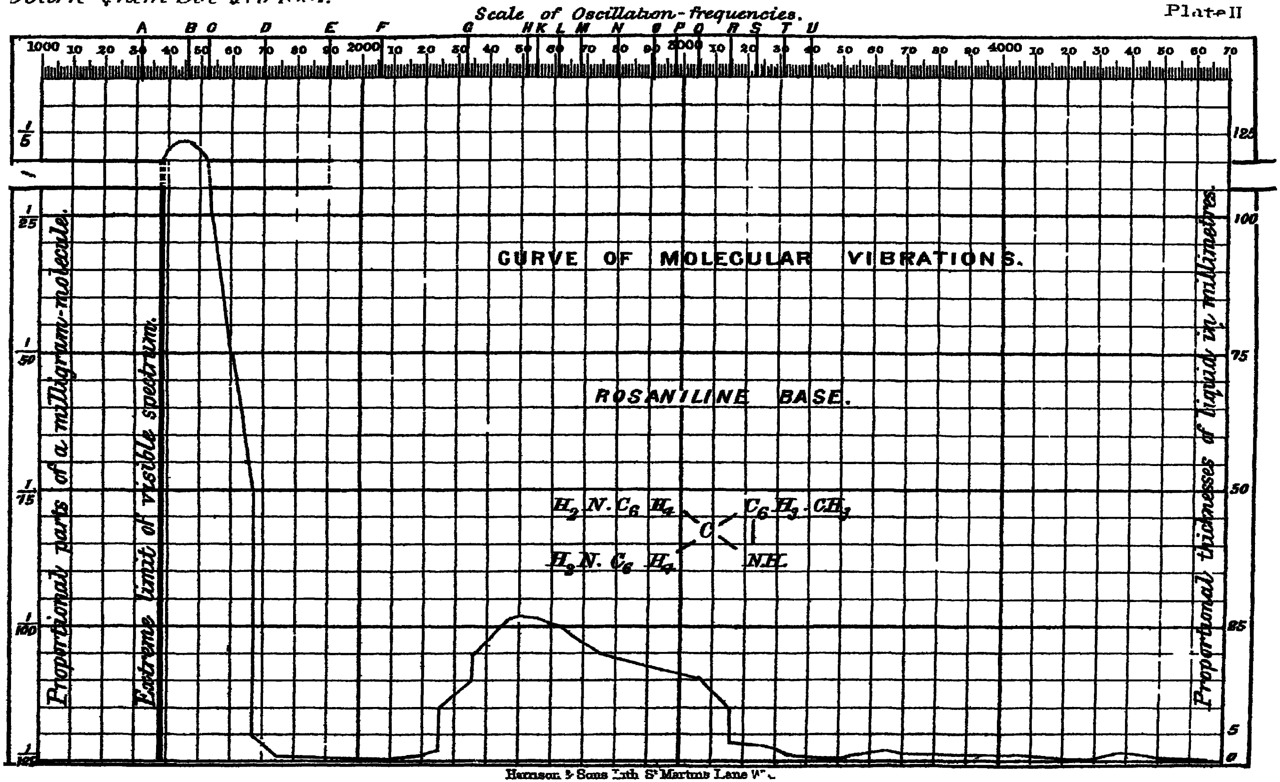
Journ Chem Soc Feb 1887



Harrison & Sons, Lith. St Martins Lane W.C.

Journ Chem Soc Feb 1887.

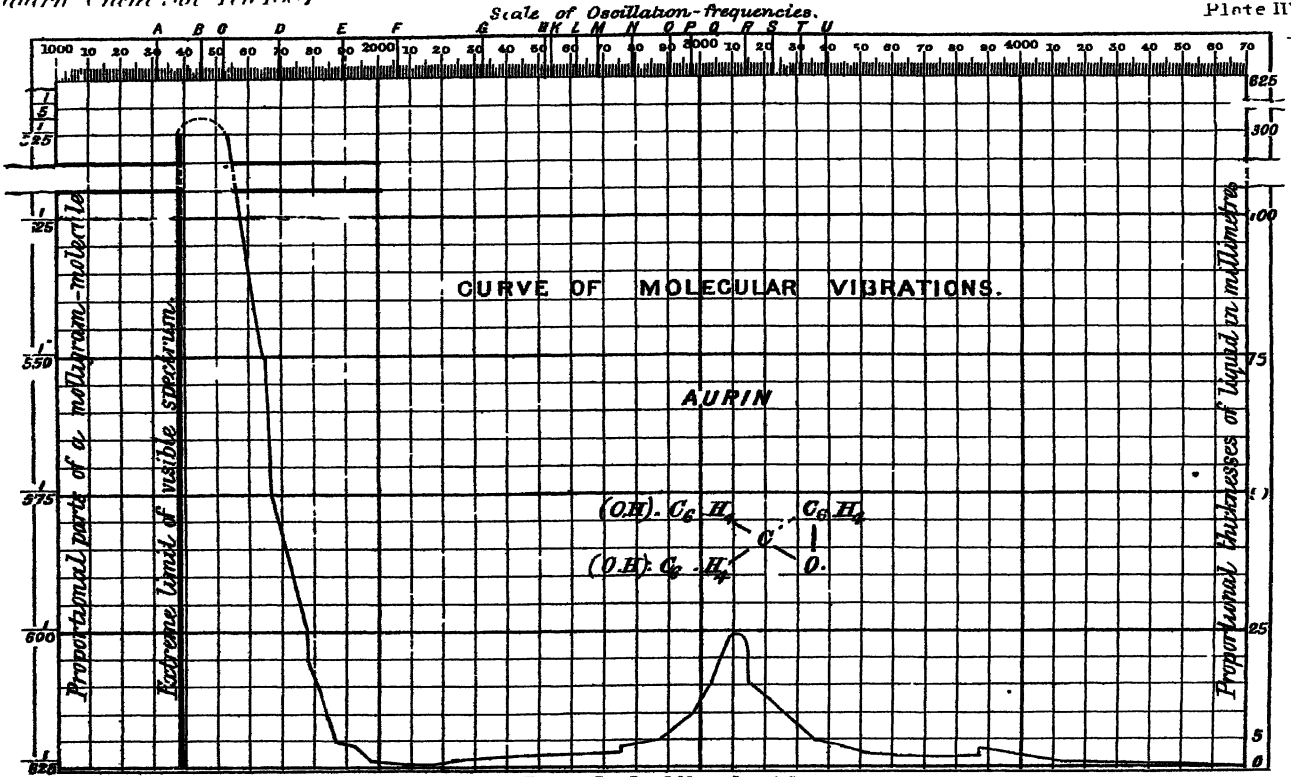
Plate II



Harrison & Sons Lith St Martins Lane W.C.

Journ Chem Soc Feb 1887

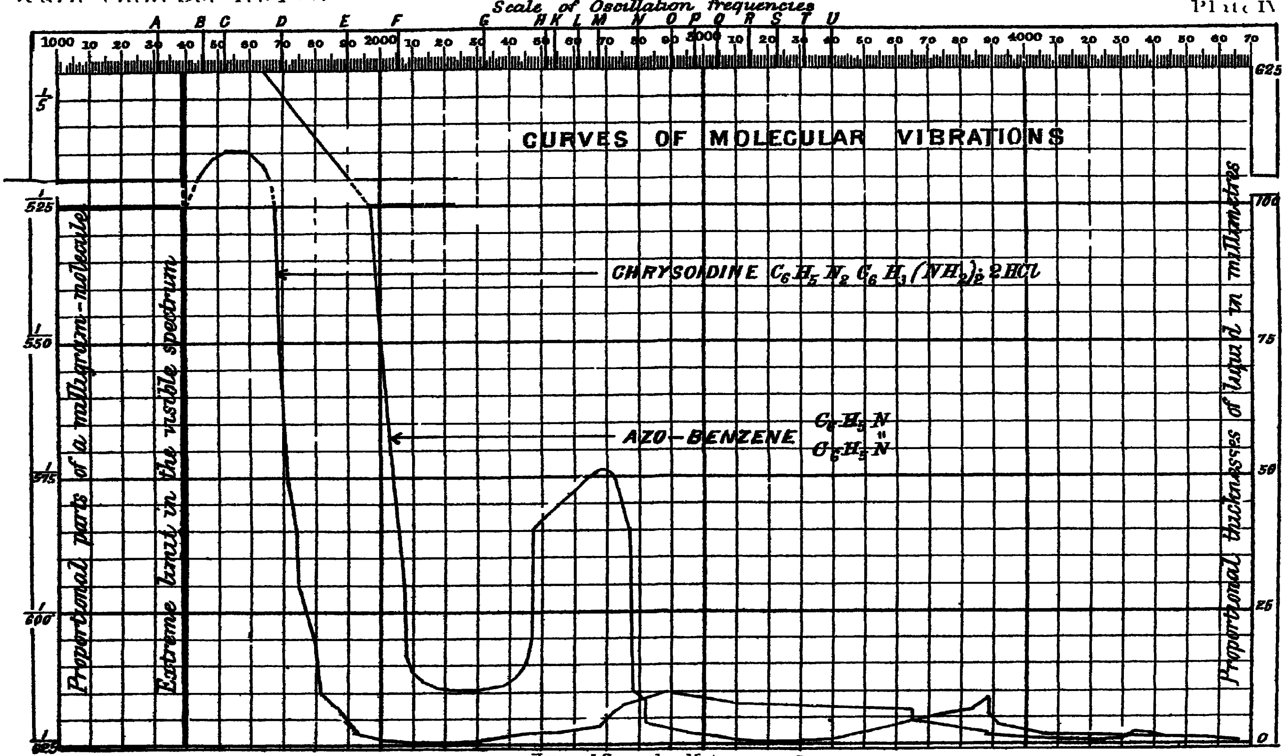
Plate II



Harrison & Sons Lith. S Martins Lane W.C.

Journ Chem Soc Feb 1887

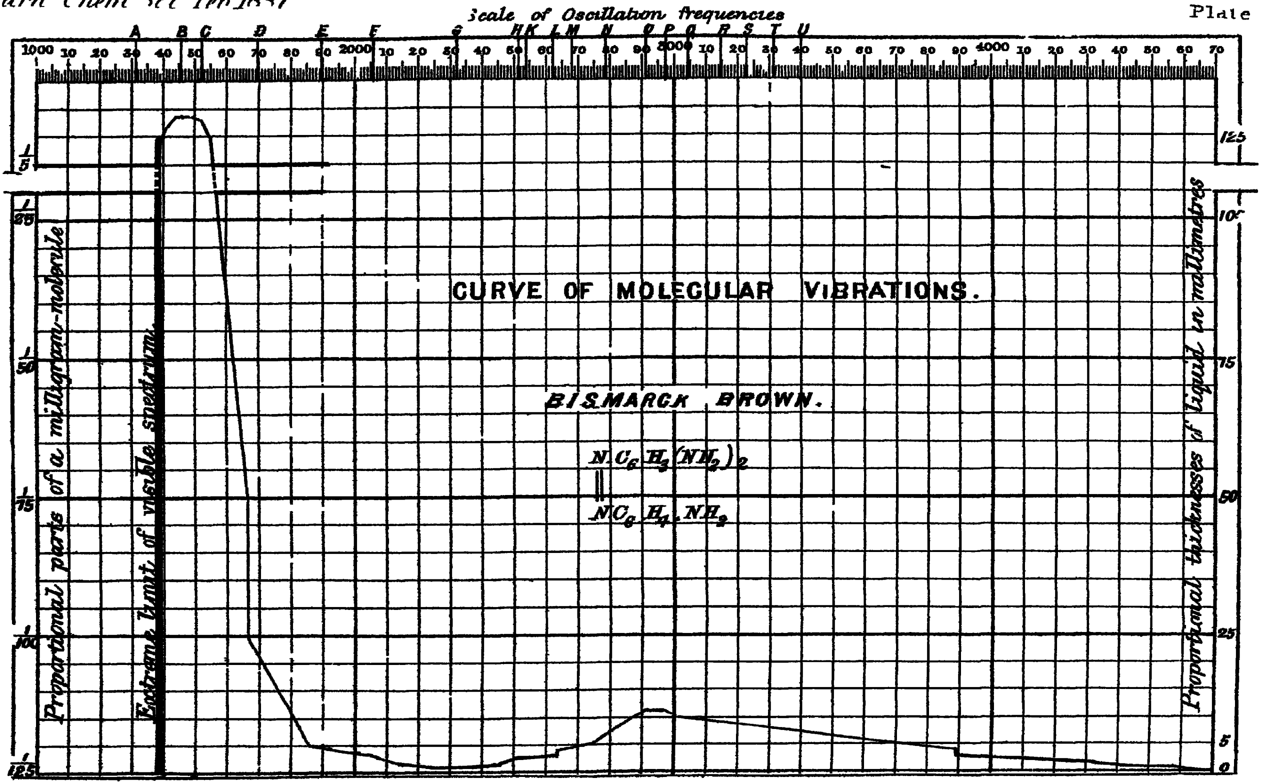
Plate IV



[illegible] Sons [illegible] Martin [illegible]

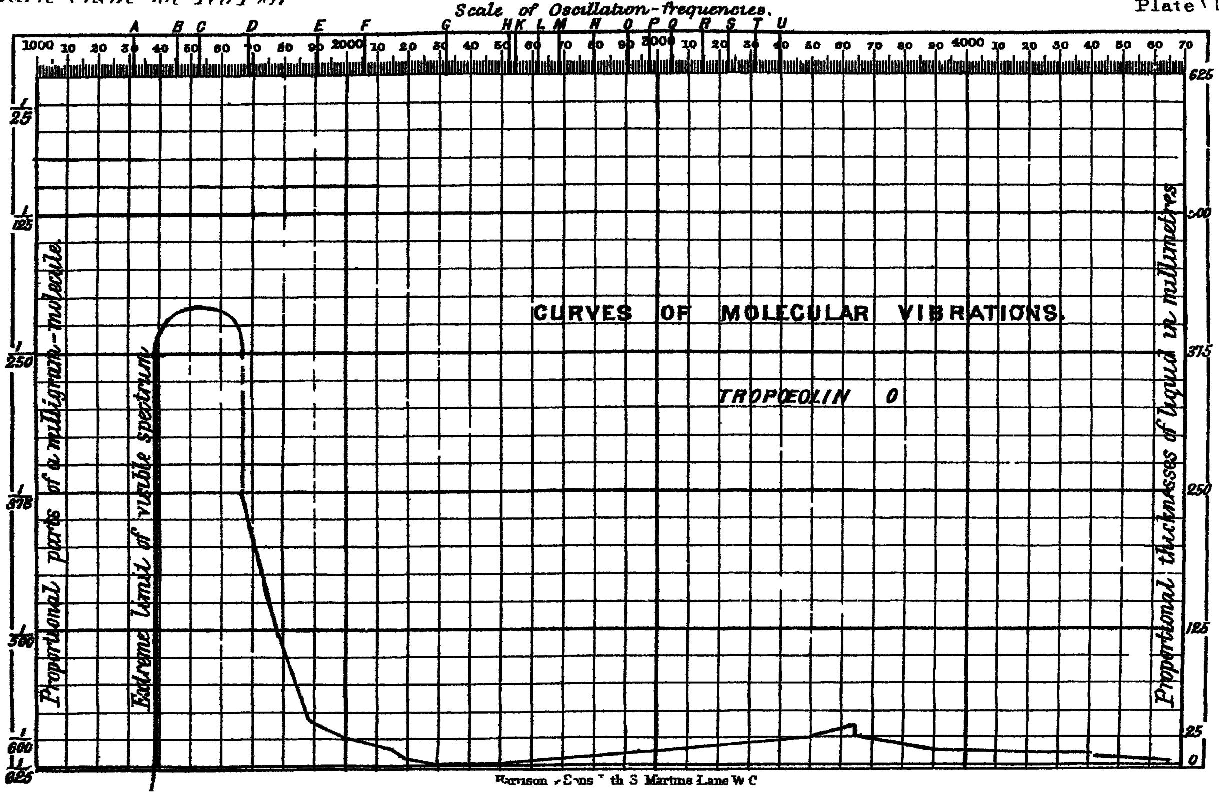
Journ Chem Soc Feb 1887

Plate

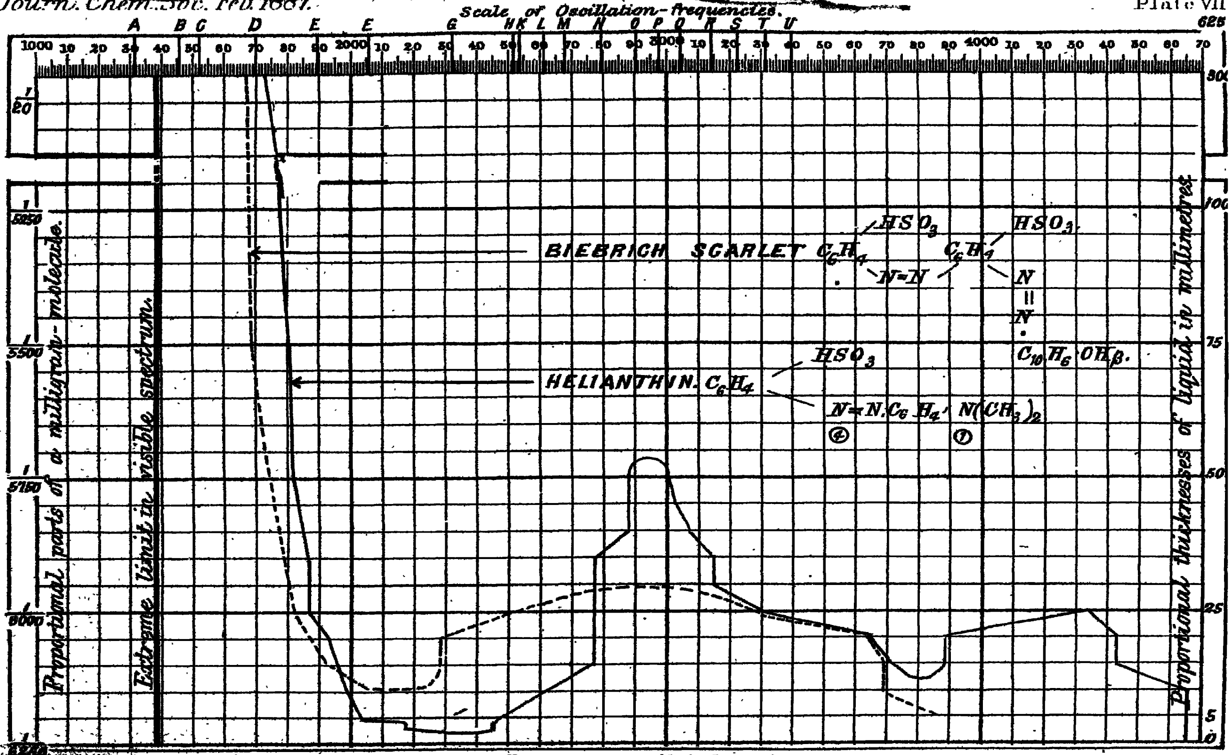


Journ Chem Soc Feb 1887

Plate VI



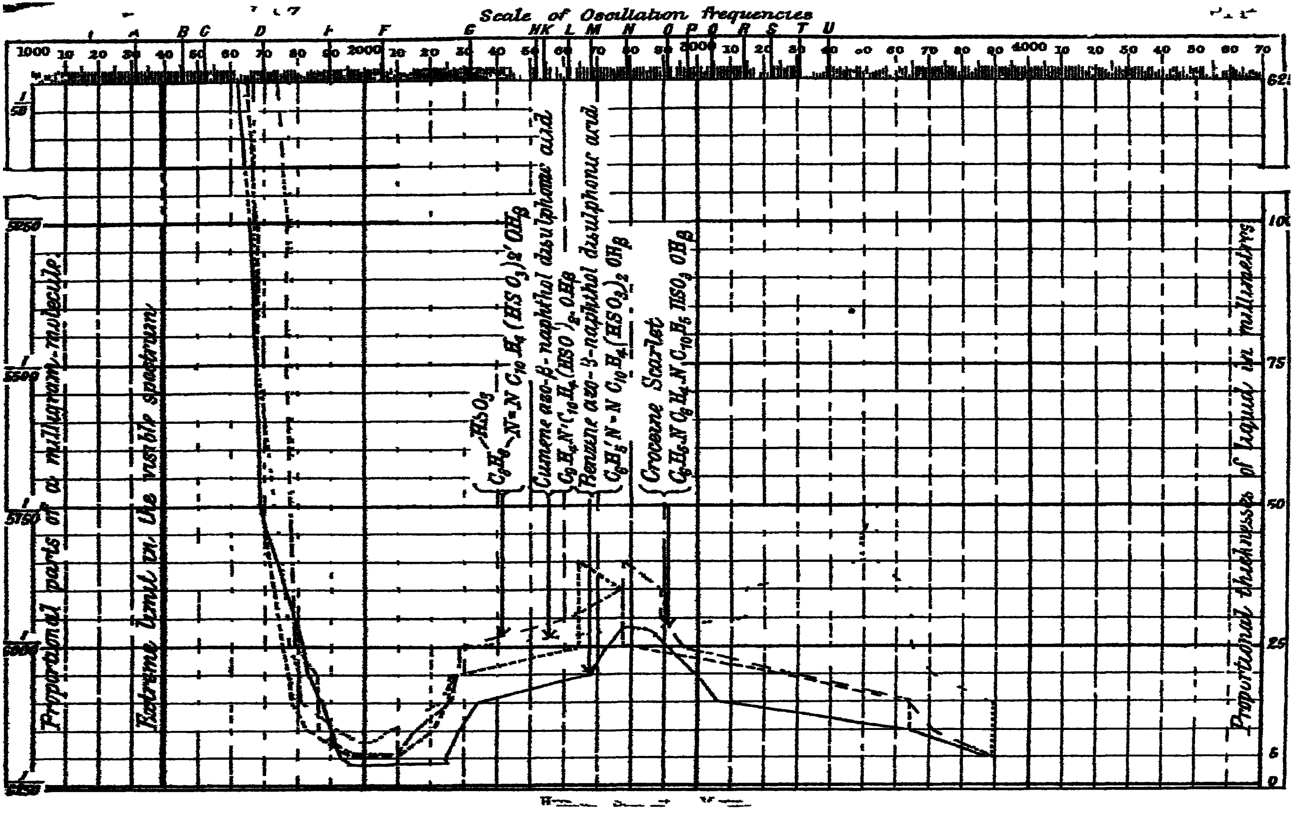
Harrison & Sons Lith St Martins Lane W C



BIEBRICH SCARLET $C_6H_4 \begin{cases} HSO_3 \\ N{=}N \end{cases} C_6H_4 \begin{cases} HSO_3 \\ N{=}N.C_{10}H_6.OH\beta \end{cases}$

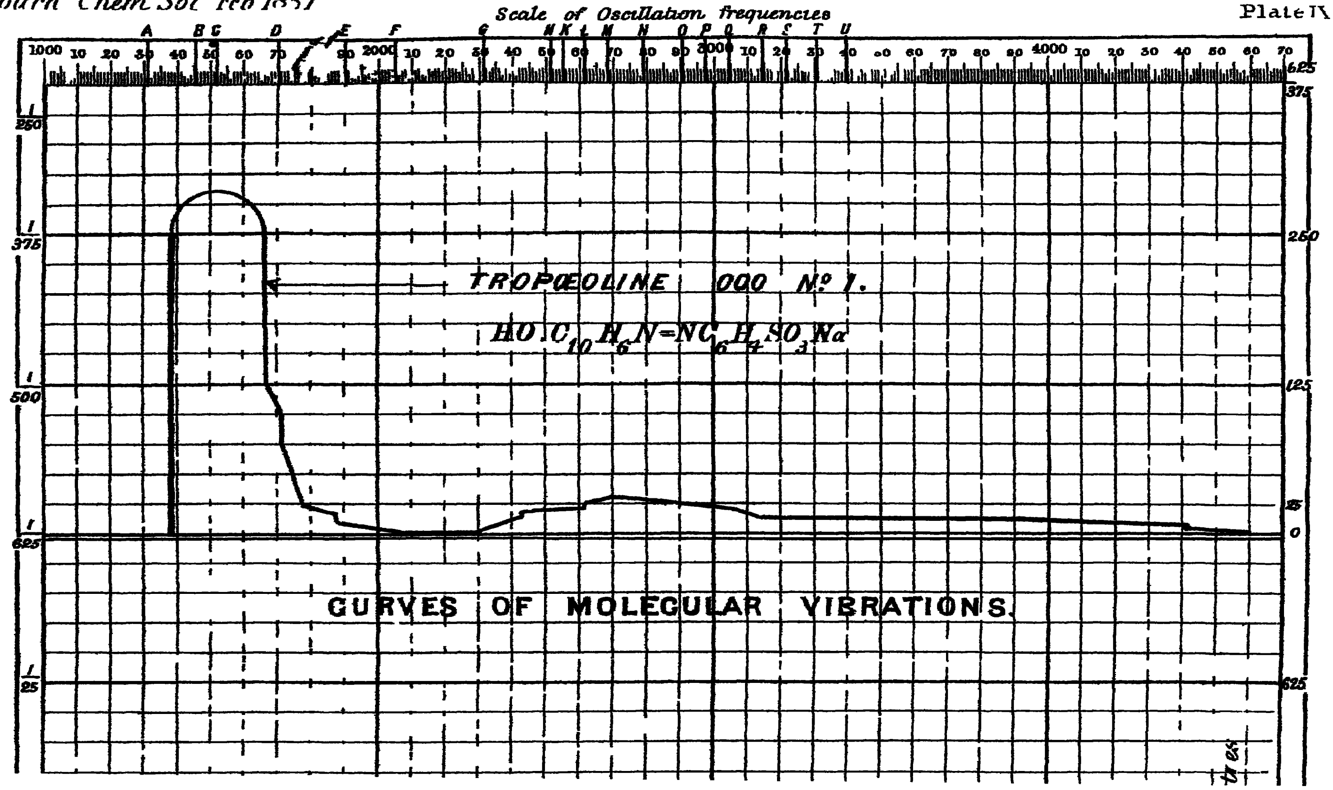
HELIANTHIN. $C_6H_4 \begin{cases} HSO_3 \\ N{=}N.C_6H_4'N(CH_3)_2 \end{cases}$ ④ ①

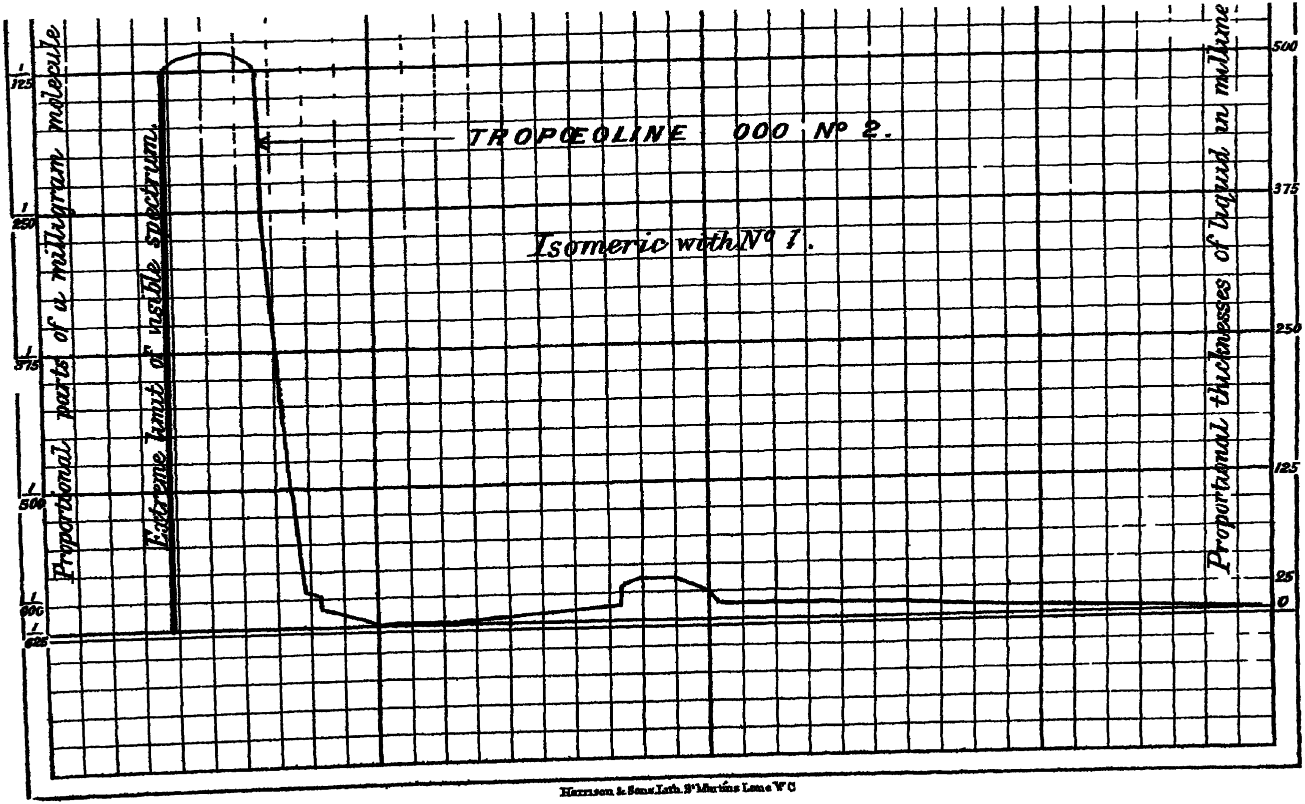
Harrison & Sons, Lith. St Martins Lane, W.C.


Scale of Oscillation frequencies
A B C D F G H K L M N O P Q R S T U
1000 10 20 30 40 50 60 70 80 90 2000 10 20 30 40 50 60 70 80 90 3000 10 20 30 40 50 60 70 80 90 4000 10 20 30 40 50 60 70
Proportional parts of a milligram-molecule
Extreme limit in the visible spectrum
Proportional thicknesses of liquid in millimetres
1/5250
1/5500
1/5750
1/6000
1/6250
1/50
100
75
50
25
5
0
625
$C_6H_3{-}HSO_3{-}N{=}N\,C_{10}H_4(HSO_3)_2'OH_\beta$
Cumene azo-β-naphthol disulphonic acid
$C_9H_{11}N'C_{10}H_4(HSO)_2.OH_\beta$
Benzene azo-β-naphthol disulphonic acid
$C_6H_5'N{-}N\,C_{10}H_4(HSO_3)_2\,OH_\beta$
Croceine Scarlet
$C_6H_5.N\,C_6H_4.N\,C_{10}H_5\,HSO_3\,OH_\beta$

Journ Chem Soc Feb 1887

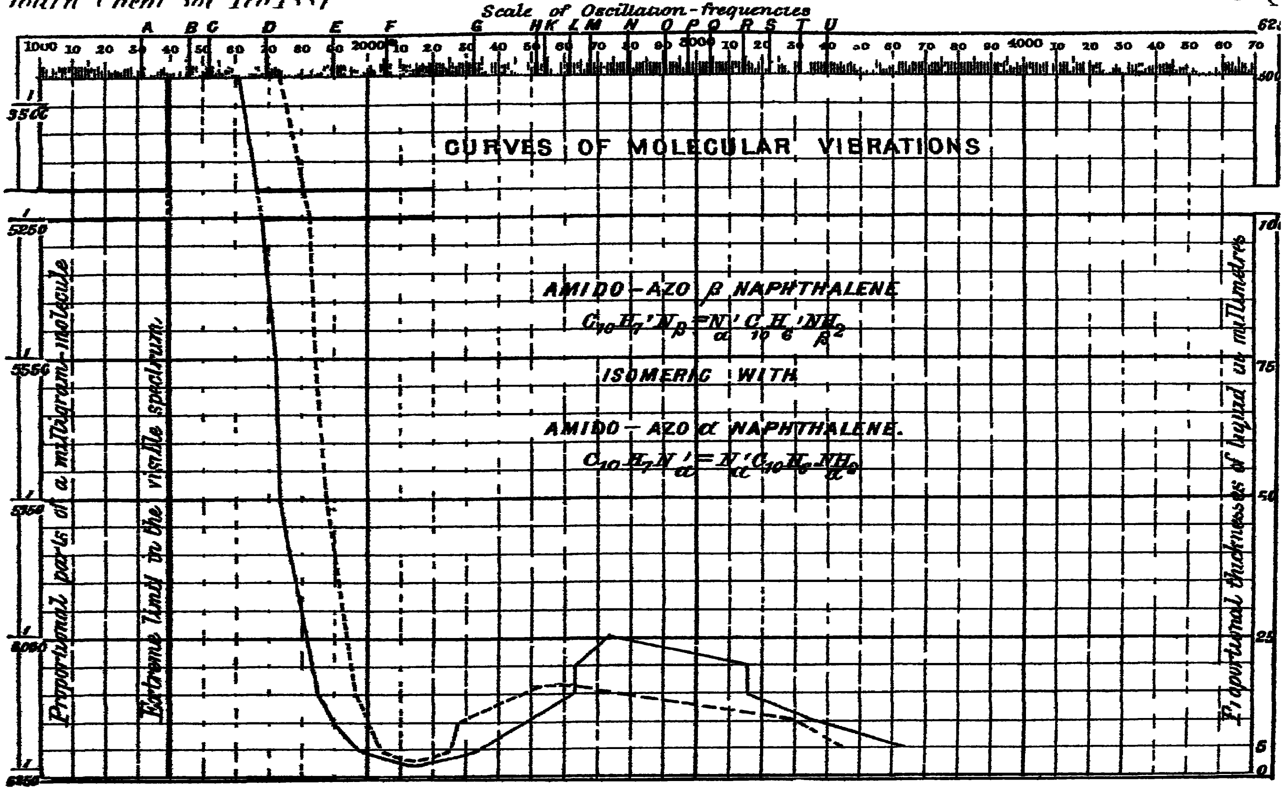
Plate IX





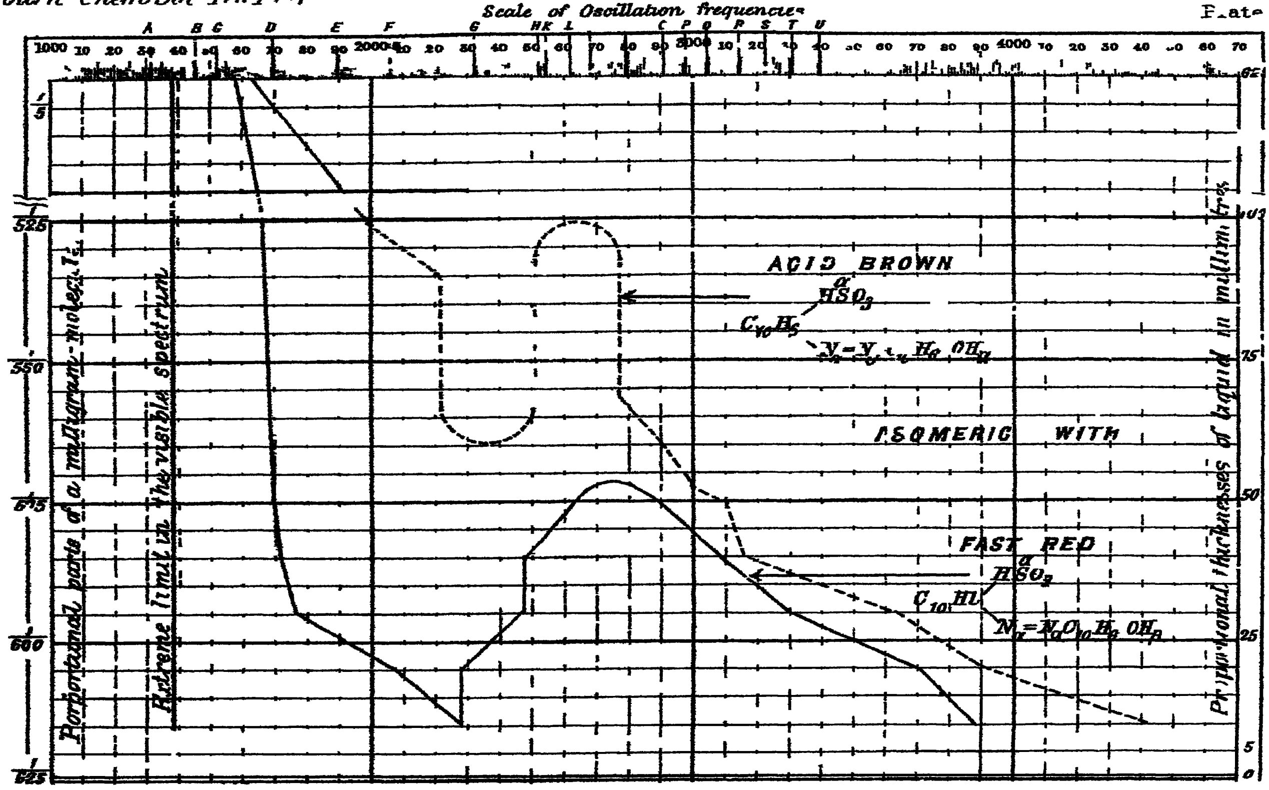
Harrison & Sons, Lith. St Martins Lane W C

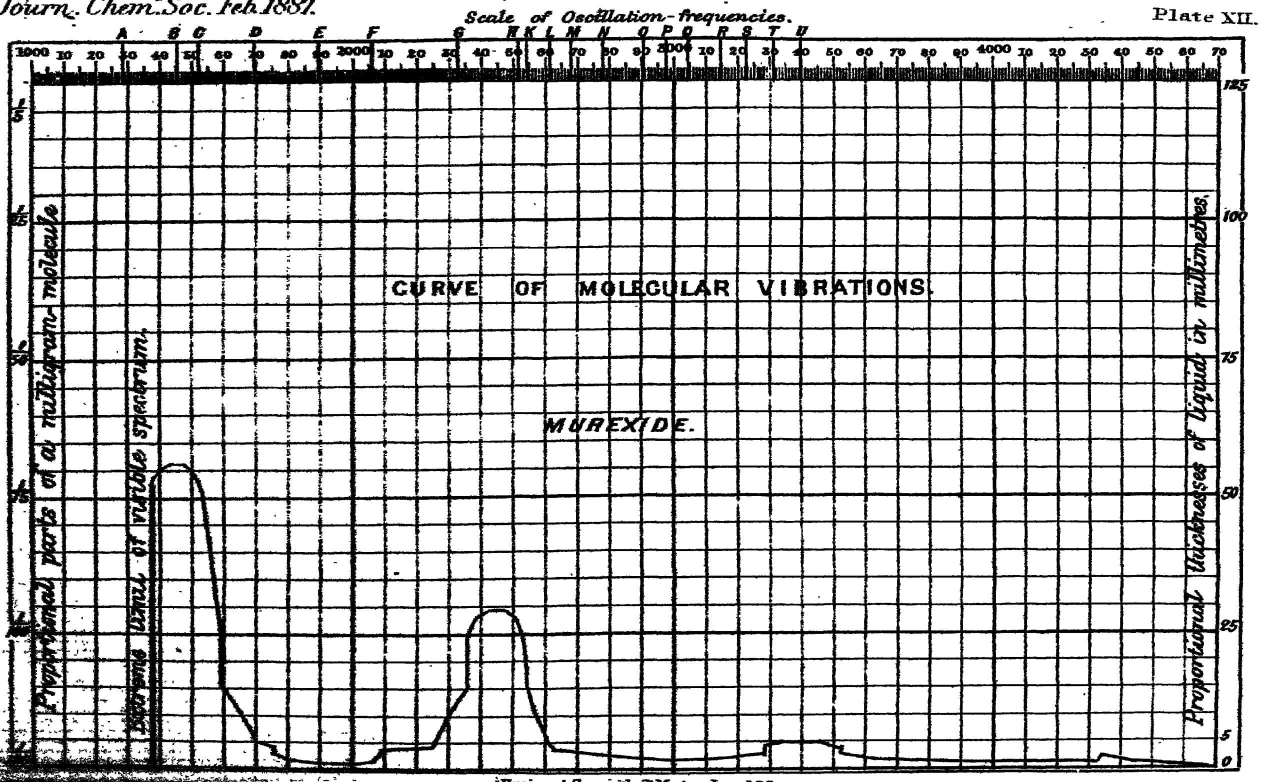
Journ Chem Soc Feb 1887



Journ Chem Soc Feb 1897

Plate





Harrison & Sons, Lith. St Martins Lane W.C.

and finely crystalline, except when marks due to imperfect rolling were observed, and which of course depended on the red shortness of the material.

Relative Hardness.—The relative hardness was determined, as in my experiments on cast iron, by means of the weight in grams necessary to produce a scratch with a diamond when drawn over the smooth surface of the metal. I have described an apparatus for this purpose, together with the method of observation, and a number of experiments with various materials, in a paper read a few days ago,* and now in course of publication. In this paper, the following conclusions are arrived at:—

1. That in substances perfectly homogeneous in structure, hardness and tenacity vary together with the number of atoms in a given space. Pure annealed metals pretty closely obey this rule.
2. That in the majority of substances which possess some crystalline or other structure, hardness and tenacity do not vary according to any simple rule. Cast iron is an excellent example of this, since hard cast iron generally has a low tenacity, and *vice versâ.*

On examining Table B (p. 142), it will be seen that in these experiments the relative hardness does not vary over wide limits, for whilst in cast iron variations of from 22 to 72 were observed (Trans., 1885, **47**, 905), in this instance the range is only from 15 to 21. The variations in hardness appear to follow in order of tenacity more than in order of silicon, and this is what might be anticipated from the fact that the metal was a near approach to pure iron. It may be mentioned that the workman in turning these specimens considered them about equal in hardness, and that another workman who prepared the smooth surfaces came to a similar conclusion. It is evident, therefore, that a difference of a few degrees on the arbitrary scale I employ is not perceptible to an ordinary workman, though if the hardest and softest had been carefully compared a difference would have been noticed. The specimen containing 0·4 per cent. of silicon and 0·21 of carbon, and which was too red short to roll, had a hardness of 24, or somewhat greater. The following list, taken from the paper previously referred to, will help to show the value of these numbers for relative hardness:—

---

* Before the Birmingham Philosophical Society.

Substances.	Relative hardness.
Steatite	1
Lead (commercial)	1
Tin "	2·5
Rock salt	4
Zinc (pure annealed)	6
Copper (pure annealed)	8
Calcite	12
Softest iron	15
Fluor-spar	19
Mild steel	21
Tyre steel	20—24
Good cast iron	21—24
Bar iron	24
Apatite	34
Hard cast-iron scrap	36
Window glass	60
Very hard white iron	72

It appears, therefore, that the presence of silicon tends to somewhat harden the metal, even when it has been slowly cooled, but this hardness is also probably very closely connected with tenacity.

Hardening Properties.—In connection with the effect of rapid cooling on the hardness of the metal, no regular series of experiments was made, though a few interesting facts were observed. The original metal was not hardened if plunged into water while hot; but it was noticed that in Ingot 11, on attempting to drill underneath the skin of the 2-inch square bar, the metal was perceptibly harder just under the skin than in the interior. This ingot contained, in addition to the silicon, 0·12 per cent. of carbon, and it is believed that hardening commenced at about this point in the series. With Ingot 13, however, which contained 0·21 per cent. of carbon and 0·40 of silicon, hardening was very marked, and a chisel was prepared which, when heated and quenched in water, cut the unhardened metal freely without itself suffering at the edge. It was very tough, and its edge is apparently uninjured after considerable rough usage. It was, however, difficult to work when hot. Punches were also made from this metal, and stood well when used.

Conclusions.—On adding silicon, in the form of silicon pig, to the purest Bessemer iron, the following results are obtained:—

The metal is quiet in the mould when a few hundredths per cent. even of silicon is added. The metal is originally red short, especially at a dull red heat, though it works well at a welding temperature;

No.	University College No	Chemical analysis.					Hot tests	Cold tests	Welding tests.
		C.	Si	S.	Mn.	P.			
1	11411	0·02	0·098	0·039	0·06	0·01	Worked well at welding heat, red short at dull red heat	Good	Perfect weld
	11778	—		-			-	-	—
2	11415	0·029	0·02	0·03	0·10	0·03	Do	Do.	Broke owing to red shortness
	11713	—							
3	11417	0·02	0·027	0·028	0·07	0·012	Do	Do	Very good weld
	11785								
4	11413	0·076	0·035	0·03	0·10	0·06	Do	Do	Do.
	11781								
5	11414	0·057	0·039	0·03	0·09	0·05	Do.	Do.	Do.
	11782							—	—
6	11412	0·052	0·08	0·036	0·09	0·06	Do.	Do.	Do.
	11779	--				—	--	—	—
7	11728	0·113	0·117	0·015	0·08	0·015	Do.	Do.	Do.
	11780		-		-	-	—	—	—
8	11416	0·031	0·13	0·033	0·09	0·08	Do.	Do.	Not so good
	11781							-	--

TABLE A.—*General Summary of Results.*

Specific extension.		Modulus of elasticity.		Limit of elasticity per square inch.		Breaking load per square inch.		Ratio of limit to break.	Extension per cent. on 10 inches.	Reduction of area per cent.	Relative hardness.	Remarks.
e_t	e_c	E_t.	E_c.	Pounds.	Tons.	Pounds.	Tons.					
0·317	0·314	31,590,000	31,870,000	28,600	12·77	48,850	21·80	0·586	21·7	76 3	18	Silky.
-	—	—	—	29,680	13·25	48,810	21·79	0·608	30·7	77·8	—	Very finely silky.
0·326	0·320	30,610,000	30,420,000	30,000	13·39	46,410	20·72	0·646	19·5	43·4	16	Fracture irregular; about 60 per cent. silky; the remainder in patches and pipes of crystal.
-		—	—	28,610	12·77	42,940	19·17	0·666	15·7	37·3	—	Very unsound and faulty; irregular crystalline spots; surface extremely distressed all over.
0·321	0·321	31,120,000	31,120,000	36,530	16·30	49,010	21·89	0·714	24·2	63·7	15	Fracture silky; but full of pipes and reedy holes in part filled with crystalline siliceous matter; some small specks of crystal.
		-	-	42,980	19·19	48,410	21·61	0·888	27·8	71·1	—	Very finely silky, but with three large and about 20 small round pipes, filled with siliceous matter which flew out in a cloud of dust on fracture; surface reedy.
0·328	0·320	30,530,000	31,250,000	33,860	15·11	51,920	23·18	0·652	15·6	30·0	17	Fracture irregular, with unsound pipes or fissures; mostly crystalline granular; edges silky.
	-	--	--	36,170	16·28	51,430	22·96	0·709	17·1	33·7	—	Like 11779, but more irregular, and surface a good deal distressed.
0·330	0·321	30,300,000	31,120,000	34,090	15·22	50,610	22·60	0·673	15·4	36·3	17	Fracture irregular and not entirely sound; about 30 per cent. finely crystalline, rest silky.
	—	—	—	39,190	17·63	53,070	23·97	0·735	21·1	39·1	—	Irregular; mostly silky, but with crystalline spots; in places unsound and reedy; surface reedy.
0·311	0·323	32,130,000	31,000,000	40,160	17·92	54,280	24·23	0·739	24·0	46·0	20	Silky, but with irregular crystalline specks and pipes.
-	—	—	—	34,780	15·53	52,050	23·21	0·668	24·5	43·8	—	Silky but irregular, with crystalline spots and pipes; surface a little distressed.
0·333	0·326	30,070,000	30,610,000	39,730	17·73	61,490	27·45	0·646	12·8	19·7	21	Fracture 65 per cent. finely crystalline, the rest half finely granular; half silky; surface very much distressed on one side.
--	—	—	—	40,920	18·27	64,180	28·65	0·638	18·4	33·9	—	Fracture about 65 per cent. finely crystalline, the rest irregular, for the most part silky; surface a good deal distressed.
0·312	0·313	32,100,000	32,000,000	41,620	18·58	57,720	25·77	0·721	22·0	47·7	20	Silky; specked with crystals and silica (yellowish crystalline material), a little reedy on surface.
-	--	—	—	40,710	18·17	57,330	25·59	0·710	17·7	36·2	—	Somewhat irregular, silky—with flattened pipes containing crystalline siliceous matter, surface a little distressed.

the red shortness is increased by silicon. In all cases examined, the metal was tough cold, and welded well, silicon having little or no influence. Silicon increases the elastic limit and tensile strength, but diminishes the elongation and the contraction of area, a few hundredths per cent. having a remarkable influence in this respect. The appearance on fracture by tensile force is changed from finely silky to crystalline, while the fracture produced by a blow gradually becomes more like that of tool steel as silicon increases. The hardness increases with the increase of silicon, but appears to be closely connected with the tenacity. With 0·4 per cent. of silicon and 0·2 per cent. of carbon, a steel was obtained difficult to work at high temperatures, but tough when cold, capable of being hardened in water, and giving a cutting edge which successfully resisted considerable hard usage.

It must be pointed out that these conclusions are only true under the circumstances of my experiments. Doubtless the results would be very much modified by the presence of varying quantities of manganese, carbon, and other elements, and it would be unwise at this stage of the work to draw any general conclusions. I am hoping, however, to pursue the investigation further, and to examine the effect of silicon on mild steel with manganese, on steel castings, and on tool steel.

It will be seen from the text how much I am indebted for assistance to Professor Kennedy, Mr. Harbord, and Mr. Walton, and without this help the experiments could not have been conducted. It is only just to these gentlemen to state that I am more in the position of one who has initiated the work, than of one who has himself been able to perform it.

XIX.—*Isomeric Change in the Phenol Series. I. The Action of Bromine on the Dibromonitrophenols.*

By Arthur R. Ling.

In a paper by Dr. Armstrong (*Jour. Chem. Soc.*, 1875, 520), entitled "Note on Isomeric Change in the Phenol Series," this author shows that parabromodiorthonitrophenol (m. p. 76°) is converted by mere warming with bromine into the isomeric orthobromoparaorthodinitrophenol (m. p. 116°). Thinking that isomeric change might also take place in other cases, Dr. Armstrong directed his attention to the dibromonitrophenols, and found as the result of a preliminary experiment that when dibrom*ortho*nitrophenol (m. p. 117°) was heated with bromine a small amount of the isomeric dibromo*para*nitrophenol (m. p. 141°) was produced, together with a considerable quantity of a non-nitrogenous compound insoluble in alkaline solutions and in alcohol, but readily soluble in benzene, from which it crystallised in yellow six-sided plates and prisms melting above 200°. The same compound was obtained when dibromo*para*nitrophenol was similarly treated.

At the suggestion of Dr. Armstrong, I have undertaken the experiments recorded in this paper with the view of obtaining, if possible, some explanation as to the mode in which the change from an orthonitroparabromo- to a paranitro-orthobromo-derivative may be assumed to take place.

The non-nitrogenous compound, which is the ultimate product of the reaction between bromine and the dibromonitrophenols, was first examined, a quantity of the substance originally prepared by Dr. Armstrong being used. Two closely agreeing bromine-determinations, together with the fact that it was found not to contain hydrogen, suggested that it was in all probability bromanil (tetrabromoquinone), $C_6Br_4O_2$, a compound first described by the late Dr. Stenhouse (*Jour. Chem. Soc.*, 1870, 6).

The numbers obtained for bromine are as follows:—

I. 0 2633 gram gave 0·4664 gram AgBr.
II. 0·2581 „ 0·4558 „

	Theory ($C_6Br_4O_2$).	Found. I.	Found. II.	Mean.
Br....	75·47 p. c.	75·54	75·32 p. c.	75·43 p. c.

Stenhouse has shown that bromanil is converted by treatment with a 4 per cent. aqueous solution of potassium hydroxide into potassium bromanilate, which is a very characteristic salt:

$$C_6Br_4O_2 + 4KOH = C_6Br_2O_2(OK)_2 + 2KBr + 2OH_2.$$

2 grams of the supposed bromanil, moistened with alcohol, was therefore added to a solution of caustic potash (2·4 grams KOH + 60 c.c. H_2O) contained in a small flask; the mixture was occasionally shaken during a period of five hours, at the end of which time the yellow crystals had disappeared, having given place to dark-purple crystals. Common salt was then added to precipitate that part of the salt which was dissolved in the alkaline solution. After being several times dissolved in water, precipitated with common salt, and finally recrystallised, the salt was obtained in a form agreeing with Stenhouse's description of potassium bromanilate:—*

---

* The sodium chloride used in the precipitation of the salt was pure, and con-

0·2469 gram gave 0·1118 K_2SO_4.

	Theory ($C_6Br_2K_2O_4 + H_2O$).	Found.
K	19·90 per cent.	20·29 per cent.

The melting point of the bromanil from the dibromonitrophenols was found to be 288°; a specimen kindly given me by Mr. Groves was found to melt at the same temperature.

The action of bromine on the dibromonitrophenols may therefore be represented by the following equation:—

$$C_6H_2Br_2(NO_2)\cdot OH + 4Br_2 + 2OH_2 = C_6Br_4O_2 + 6HBr + HNO_3.$$

In order to throw light on the apparent isomeric change involved in the production of dibromoparanitrophenol, it was deemed expedient to try, first of all, the action of a mere trace of bromine on dibromorthonitrophenol; for this purpose the following experiments were made:—

I. 10 grams dibromorthonitrophenol was introduced into a bottle together with about 40 c.c. water and bromine in the proportion of $C_6H_2Br_2(NO_2)OH : \frac{1}{10}Br_2$; the stopper was then inserted, wired down, and the bottle heated in a pan of boiling water. The heating was continued for 3½ hours.

There was no change apparent, the product being entirely soluble in potassium carbonate solution, and giving only the red crystals of potassium dibromorthonitrophenol; these on treatment with acid gave a nitro-derivative which melted at the same temperature as before, viz., 117°.

II. 10 grams of the substance was heated with half a molecular proportion of bromine for three hours. A small quantity of bromanil, however, was obtained; the portion soluble in potassium carbonate solution appeared to be the unaltered nitro-compound; it melted as before at 117°.

III. 10 grams of the substance was heated with one molecular proportion of bromine for five hours. The insoluble portion being removed, red crystals of the apparently unchanged substance were deposited; these were not further examined. From the mother-liquors, however, some red crystals were obtained, which it could be discerned were contaminated with a yellow salt; as the quantity of the latter was very small, separation was not attempted.

IV. 10 grams of the substance was heated with one molecular proportion of bromine for 12½ hours. The liquid filtered from the insoluble compound deposited a brownish-yellow salt. No trace of

---

tained no calcium or magnesium salts; the precautions recommended by Dr. Stenhouse were not observed.

the red salt which dibromorthonitrophenol yields was observed. A determination of potassium in the salt thus obtained gave K = 16·44 per cent. After recrystallisation, the following numbers were obtained:—

0·3098 gram gave 0·0972 gram K_2SO_4 = 14·04 per cent. K.
0·2619 gram gave 0·1854 gram AgBr = 30·20 per cent. Br.

It was obvious from these numbers that I was dealing with anything but a pure compound; they clearly point, however, to the presence of a potassium monobromonitrophenol.

It appeared probable from the foregoing experiment that the alkaline extract must have contained a mixture of salts. Several experiments were therefore carried out under the same conditions as the last mentioned, in order to prepare a larger quantity of product. As the result of several such experiments, I not only obtained a quantity of a substance having much the same appearance as before, but ultimately by means of fractional crystallisation and purification with animal charcoal, I succeeded in isolating from the mixture, the salts of the three following compounds in a state of purity:—

	M. p.
Orthobromodinitrophenol................	116°
Orthobromoparanitrophenol..............	102
Dibromoparanitrophenol	141

A small quantity of potassium bromanilate was also separated, which was undoubtedly produced by the action of potassium carbonate on the bromanil.

The numbers obtained on analysing the above-mentioned salts are as follows:—

Potassium Bromodinitrophenol.

0·2273 gram gave 0·652 gram K_2SO_4.

	Theory ($C_6H_2BrN_2O_5K$).	Found.
K........	12·95 per cent.	12·84 per cent.

It was found to be exceedingly difficult to obtain good numbers for bromine in this salt, as it is very apt to deflagrate when heated with lime in a tube, thereby causing a loss of bromine. A determination of bromine was therefore made in the phenol:—

0·1483 gram gave 0·1062 gram AgBr.

	Theory ($C_6H_3BrN_2O_5$).	Found.
Br........	30·42 per cent.	30·54 per cent.

Potassium Bromoparanitrophenol.

0·2078 gram gave 0·0720 gram K_2SO_4.
0·1890 gram gave 0·1359 gram AgBr.

	Theory ($C_6H_3BrNO_3K$).	Found.
K........	15·23 per cent.	15·54 per cent.
Br........	31·25 „	30·64 „

That this salt was potassium bromo*para*nitrophenol was proved by the fact that on treating the phenol from it, dissolved in glacial acetic acid, with bromine, dibromoparanitrophenol was obtained, which was identified by taking the melting point and by converting it into the potassium-derivative, the light yellow crystals only being obtained.

Potassium Dibromoparanitrophenol.

It was unnecessary to analyse this salt; the compound obtained on treatment with acid being sufficiently characterised by its behaviour on heating, sharply melting with decomposition at 141°. Furthermore, it was previously obtained by the same means by Dr. Armstrong, as stated in the paper before referred to.

About two-thirds of the crude mixture of salts consisted of potassium bromodinitrophenol; the remainder was chiefly potassium bromoparanitrophenol, potassium dibromoparanitrophenol being the least abundant.

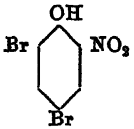
In order to determine approximately the amount of bromanil formed, two rough experiments were made with dibromorthonitrophenol, and one with dibromoparanitrophenol. 10 grams dibromorthonitrophenol was heated as before with 5·5 grams bromine. The crude bromanil was collected on a filter and weighed: 4·5 grams was the weight found. Theoretically there should have been only 3·6 grams. In the second experiment 10 to 11 grams bromine was used; 9·5 grams crude bromanil was obtained, the theoretical amount being 7·2 grams. 10 grams dibromoparanitrophenol, heated with 5·5 grams bromine, yielded 3·3 grams crude bromanil, being just under the weight required by theory.

The alkaline extract from this last experiment was found to consist of a mixture of the same salts in about the same proportions as that obtained from dibromorthonitrophenol.

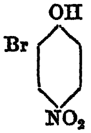
In each case, the bromine had almost all disappeared, and a considerable amount of gas—nitric oxide—escaped on releasing the stopper of the bottle.

The foregoing results serve both to confirm and to extend Dr. Armstrong's conclusion that the action of bromine on dibrom*ortho*-

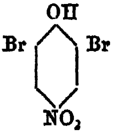
nitrophenol is attended with isomeric change, for not only has dibromo*para*nitrophenol been obtained, but also monobromo*para*nitrophenol.



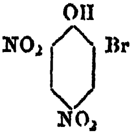
Dibrom*orth*onitritrophenol.



Bromo*para*nitrophenol.



Dibromo*para*nitrophenol.



Bromodinitrophenol.

The production of the latter shows also that the formation of bromanil takes place partly at the expense of the bromine of the dibromonitro-compound, a conclusion in harmony with the fact that more bromanil is obtained than corresponds with the amount of bromine used, although it must not be forgotten that the nitric acid which, it may be presumed, is initially formed from the NO_2 displaced, would serve to render a considerably larger amount of the bromine available than is indicated by the equation previously given. The experiments throw no light on the precise manner in which the isomeric change takes place; but the conditions are such that it would appear to be almost beyond question that it is a case of true intramolecular change.

I purpose extending my experiments to other nitro-halogen phenol-derivatives, in the hope of obtaining further evidence in explanation of the isomeric change.

In conclusion, I have to express my thanks to Professor Armstrong for the many valuable suggestions, and the great help he has given me whilst engaged in this work.

XX.—*Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra.* Part VIII. *A Study of Coloured Substances and Dyes.*

By W. N. Hartley, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

In a paper which was read before the Chemical Society in 1876 by Dr. Otto Witt, and which is published in the *Berichte*, 9, 522, a statement is made to the following effect:—"Whilst neither benzene nor its nitro-, amido-, nor hydroxy-derivatives are colouring matters, we find that the nitranilines and nitrophenols belong to this class;

but they become colourless when acetyl is introduced into the former, or an alcohol radical replaces in the latter the hydrogen of the hydroxyl. From this, it follows—

"That the tinctorial character of aromatic compounds is conditional upon the simultaneous presence of a colour-producing group and a salt-forming group in the molecule.

"A group of atoms of the former kind may be termed a *chromogen* and of the latter a *chromophor.*

"For instance, NO_2 is the *chromophor* of nitraniline and nitrophenol, but nitrobenzene is the *chromogen* of these bodies.

"The different nitro-diphenylamines are all acids and dye-stuffs, and their tinctorial power increases with the number of nitroxyls."

It appeared to be of interest to study the relation of the hydrocarbons to the more complex compounds which are colouring matters derived therefrom. If a source of light emits all luminous and invisible vibrations capable of being transmitted through 3 feet of air, a perfectly colourless substance will transmit these rays without impairing their intensity. A coloured substance is one which absorbs rays at either end of the spectrum, or selects rays of a certain wave-length from the middle of the spectrum. Every fluorescent substance is therefore coloured, and benzene, benzenoïd hydrocarbons, phenols, and other derived compounds which exhibit selective absorption of the ultra-violet rays are coloured: the subtlety of the colour, however, is such that the eye cannot appreciate it. That which in the ordinary acceptation of the term is a coloured substance is one in which the absorption of rays extends into a region limited by the red and violet ends of the spectrum, or between wave-lengths of 7000 and 4000 tenth-metrets. According to this view there are colours visible and invisible.

Bands of selective absorption appear to be the effect of vibrations taking place within the molecule of a substance, and these are dependent upon the rate of the vibration of the molecules themselves; they are called in general molecular vibrations. If then we desire to convert a substance such as benzene into a compound with a visible colour, it is necessary to slacken its rate of vibration so that the molecule will absorb rays with oscillation frequencies occurring within the limits of visibility.

That which has been called a chromogen is an invisibly coloured substance, and that which is termed a chromophor is an atom or a group of atoms capable of so reacting as to reduce the rate of vibration of the molecule, with the result that it absorbs rays within the limits of visibility. Under certain conditions of combination, oxygen and nitrogen are chromophors, hence also hydroxyl and nitroxyl. Oxygen and nitrogen also when united in a certain manner, to carbon, as in uric acid, form a chromogen which is readily modified into murexide. The molecules of oxygen and of nitrogen are colourless and non-absorbent in thin layers up to 3 feet of gas at atmospheric pressure, but the molecule of ozone is blue, and that of NO_2 is brown, even in very thin layers. Hydrogen peroxide, nitric acid, and to some extent hydroxylamine salts, absorb the ultra-violet rays, they are therefore invisibly coloured.* In fact, the salt-forming groups NO_2 and OH are themselves coloured either visibly or invisibly, and we can therefore readily understand how they can act as chromophors. The condensation of oxygen in compounds tends to the formation of intensely coloured substances, the feeble colours of ferrous and manganous salts become deep and intensely powerful in ferrates, manganates, and permanganates. PbO is yellow, Pb_3O_4 is red, and PbO_2 is puce-coloured.

When two benzene molecules are doubly linked by two nitrogen-atoms as in azobenzene, their mode of vibration is profoundly modified, and a brilliant colour as low down in the scale as the yellow rays is the result. A similar modification takes place when two atoms of hydrogen in benzene are replaced by two atoms of oxygen as in quinone, which is of a golden colour.

The effect of linking two or more benzene nuclei by carbon-atoms has been dealt with in a former paper, the colours are not rendered visible but the molecular vibrations are greatly reduced in rapidity.

The chromophoric properties of oxygen-atoms when united in a certain manner to carbon, and especially to benzene nuclei, are strikingly illustrated by the constitution and properties of the phenol colours, such as resorcin-phthalein, &c.

The changes introduced by oxygen- and nitrogen-atoms in quinone, the phenol colours and azobenzene, which involve the production of colours and dyes, depend upon the selective actinic absorption exerted by the benzene nucleus being reduced to visibility, that is to say, the rate of vibration of the molecule is diminished until it is less than that indicated by violet light.

The molecular vibrations of a number of nearly related dyes and coloured substances have been studied, the names and constitutional formulæ of which are given. The recorded measurements from which diagrams were drawn are first those of the visible rays, secondly those of the ultra-violet. The spectroscope used for the visible rays was furnished with a compound prism capable of separating the two D lines, the telescope moved on a divided arc, and a pointer in the eye-piece served to indicate the edges of the bands of absorption. The metallic lines of flame and spark spectra given in the Reports of the British Association, 1881, p. 320, were employed for converting arc-readings into wave-lengths, and oscillation frequencies. The rays extending from the blue into the extreme ultra-violet were examined according to the method of working described in the *Proc. Roy. Soc.*, **33**, 1 (Abstract). In order to facilitate reference, the diagrams have been drawn with the solar lines inserted in the scale of oscillation frequencies, and extending from A in the extreme red to U in the ultra-violet. The solutions were made and examined as before (see Trans., 1885, 685).

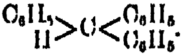
---

* There is some probability that ammonia is a substance which absorbs the ultra-violet rays, and that this is due to the nitrogen it contains. We know that all ammonia solutions show an absorption-band, even volcanic ammonia, but it has never been proved that this is not caused by some slight impurity. (See Fig. 5, Plate XXV, *Phil. Trans.*, 170, 1879.)

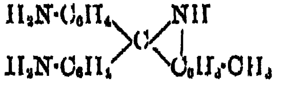
Generally speaking, absorption-bands in the ultra-violet region may be measured to four figures, that is to say, to tenth-metrets of wave-length, for not only are the bands sharply defined but they are frequently edged by the very numerous metallic lines in the spectrum employed. Measurements in the visible spectrum are not so accurate, and therefore the numbers throughout have been uniformly reduced to three figures. On the spectroscope used, the value of *minutes of arc* in oscillation frequencies and wave-lengths at A is a difference of 25 tenth-metrets of wave-length, or 6 in oscillation frequencies; at D it is 14 tenth-metrets or 4 in oscillation frequencies; at F 6 tenth-metrets or 3 in oscillation frequencies. The region at G is included in the photographs taken for the ultra-violet spectrum.

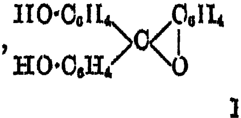
Names and Formulæ expressing the Constitution of the Substances examined.

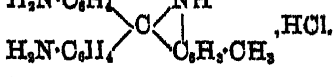
Triphenylmethane and its Derivatives.

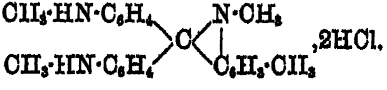
Triphenylmethane,


$$\begin{matrix}C_6H_5\\H\end{matrix}>C<\begin{matrix}C_6H_5\\C_6H_5\end{matrix}.$$

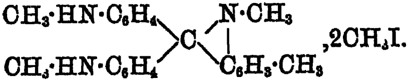
Rosaniline base,

.

Aurin,


Rosaniline hydrochloride,


Trimethylrosaniline hydrochloride, (*Hofmann's Violet*),


Trimethylrosaniline di-methyl-di-iodide, (*Iodine Green*),



Azobenzene and Derivatives.

Azobenzene, $C_6H_5·N:N·C_6H_5$.

Metadiamidoazobenzene hydrochloride, (*Chrysoidine*),
$C_6H_5·N:N·C_6H_3(NH_2)_2,2HCl$.

Triamidoazobenzene, (*Bismarck Brown*),
$C_6H_4·NH_2·N:N·C_6H_3(NH_2)_2$.

Sodium metadioxyazobenzenesulphonate, (*Tropæolin* O),
$NaSO_3·C_6H_4·N:N·C_6H_3(OH)_2$.

Sulphobenzene-azodimethylamidobenzene, (*Helianthin*),
$HSO_3·C_6H_4·N:N·C_6H_4·N(CH_3)_2$.

Benzene-azo-β-naphtholdisulphonic acid,
$C_6H_5·N:N·C_{10}H_4(HSO_3)_2·\underset{\beta}{OH}$.

Sulpho-xylene-azo-β-naphtholdisulphonic acid,
$HSO_3·C_8H_8·N:N·C_{10}H_4(HSO_3)_2·\underset{\beta}{OH}$.

Cumene-azo-β-naphtholdisulphonic acid,
$C_9H_{11}·N:N·C_{10}H_4(HSO_3)_2·\underset{\beta}{OH}$.

Phenylazo-phenyl-β-naphtholsulphonic acid, (*Croceine Scarlet*),
$C_6H_5·N:N·C_6H_4:N·C_{10}H_5(HSO_3)·\underset{\beta}{OH}$.

Biebrich Scarlet, $HSO_3·C_6H_4·N:N·C_6H_4(HSO_3)·N:C_{10}H_6·\underset{\beta}{OH}$.

Isomeric Compounds.

Isomers.
Sodium α-naphthol-azophenylsulphonate,
$OH·\underset{\alpha}{C_{10}H_6}·N:N·C_6H_4·SO_3Na$.
(Tropæolin 000 No. 1.)
Sodium β-naphthol-azo-phenylsulphonate,
$OH·\underset{\beta}{C_{10}H_6}·N:N·C_6H_4·SO_3Na$.
(Tropæolin 000 No. 2)

Isomers.
Amidoazo-β-naphthalene, $C_{10}H_7·\underset{\beta}{N}:\underset{\alpha}{N}·C_{10}H_6·\underset{\beta}{NH_2}$.
Amido-azo-α-naphthalene, $C_{10}H_7·\underset{\alpha}{N}:\underset{\alpha}{N}·C_{10}H_6·\underset{\alpha}{NH_2}$.

Isomers.
α-Naphthol-azonaphthylsulphonic acid, (*Acid Brown*),
$\underset{\alpha}{OH}\cdot C_{10}H_6\cdot \underset{\alpha}{N} : \underset{\alpha}{N}\cdot C_{10}H_6\cdot \underset{\alpha}{HSO_3}$.
β-Naphthol-azonaphthylsulphonic acid, (*Fast Red*),
$\underset{\beta}{OH}\cdot C_{10}H_6\cdot \underset{\alpha}{N} : \underset{\alpha}{N}\cdot C_{10}H_6\cdot \underset{\alpha}{HSO_3}$.

By referring to the statement of the substances examined and to the diagrams, the variations in the constitution of the different colours can be compared with variations in their optical properties.

It may be remarked that the modification seen in the curve of benzene when methyl is substituted for hydrogen, consists in three out of the four absorption-bands being merged in one, and the rate of vibration of the rays absorbed is less.

When a compound like triphenylmethane is examined the absorption curve has much of the general character of that of benzene, but the modifications which it has undergone are much like what one might expect from its constitution. First, there is one broad absorption-band, with just an indication of a second one being merged in this. Secondly, great increase in the amplitude of the vibrations is to be observed. Thirdly, the rate of vibration of the absorbed rays is greatly reduced.

In the case of benzene, we find that though its absorption of the ultra-violet rays is very great, yet this is as nothing compared with that of three benzenes linked by a carbon-atom as in triphenylmethane. Thus a milligram-molecule of benzene begins to transmit rays with oscillation frequencies 3760 and 4330, while $\frac{1}{125}$ of a molecule transmits all rays as far as 4650. (Plate I.)

With triphenylmethane, a milligram-molecule transmits nothing beyond H or oscillation frequency 2510; $\frac{1}{3125}$ of a molecule transmits rays as far as 4600. This difference results from the linking of three benzene nuclei by a carbon-atom.

The imide- and amide-groups introduced to form rosaniline base cause the molecule to absorb all rays beyond C, or 1250 oscillation frequencies. $\frac{1}{100}$ of a molecule causes an absorption near D, 1670, extending to near H, or 2450 oscillation frequencies, while $\frac{1}{125}$ of a molecule transmits all rays to 4600. (Plate II.)

If the triphenylmethane has hydroxyls, as in aurin, instead of amido- and an imide-group, then its absorptive power is greater. $\frac{1}{325}$ of a molecule absorbs all beyond C or 1520, while $\frac{1}{625}$ absorbs as far as D, 1670; $\frac{1}{500}$ of a molecule absorbs from 1780 to between Q and R, or 3100, and $\frac{1}{125}$ transmits what is practically the whole spectrum. (Plate III.)

It is obvious that here the hydroxyl is the more powerful chromophor. The greatest effect, however, is caused by the imide- and amide-groups forming a salt with hydrochloric acid, as in rosaniline hydrochloride.

A molecule of rosaniline hydrochloride absorbs all rays beyond C or between B and C; 1500 oscillation frequencies; $\frac{1}{3025}$ of a milligram-molecule absorbs all rays beyond 1600, between B and C; $\frac{1}{1050}$ absorbs all from 1600 to near H or 2500; while $\frac{1}{3125}$ transmits all rays to 4600. Triphenylmethane presents a curve not unlike that of rosaniline hydrochloride, but it begins to transmit rays somewhat earlier; that is to say, with $\frac{1}{2125}$ of a molecule. By introducing methyls into rosaniline salts, as in Hofmann's violet, the opacity of the liquid is increased; it begins to transmit red rays with little more than $\frac{1}{2500}$ of a milligram-molecule; with $\frac{1}{3000}$ it transmits from 1500 near C to 2500 near H, and absorbs all beyond; with $\frac{1}{3050}$ of a molecule, it transmits rays between G and H; while $\frac{1}{3125}$ transmits all to 4400. On the introduction of two methyl iodides into the molecule of trimethyrosaniline, so as to form iodine-green, there is a complete absorption of rays as far down as 1350 oscillation frequencies. $\frac{1}{2950}$ of a molecule transmits rays between 1350 and 1390; the absorption then continues to F, 2050; rays are transmitted from 2050 to 2200; absorption occurs again until near N, 2780, and transmission to near O, 2890. With $\frac{1}{3125}$ of a molecule, all rays are transmitted to 4600. (Plate I.)

By means of these curves, the properties of the dyes which confer upon them tinctorial powers, are easily studied.

In the examination of azobenzene, it is seen that one-fifth of a milligram-molecule transmits the visible rays as far as a point lying between C and D, or 1625 oscillation frequencies; $\frac{1}{525}$ of a molecule transmits to between E and F, or 1970 oscillation frequencies; $\frac{1}{575}$ of a molecule transmits to between E and F, or 2020 oscillation frequencies; then occurs an absorption as far as M, or 2690 oscillation frequencies; $\frac{1}{510}$ of a molecule transmits to just beyond F, or 2090; then occurs an absorption to between G and H, or 2470; rays are then transmitted to near N, or 2780, after which there is but little absorption at $\frac{1}{520}$ of a molecule, and that lies at about 3900 oscillation frequencies. In chrysoidine, the rate of the vibrations is much reduced, and their amplitude is increased. There is, with $\frac{1}{510}$ of a molecule, complete absorption of all rays lying beyond a point equidistant between D and E, or about 1800 oscillation frequencies. What appears below this point is an absorption-band, apparently the principal band of azobenzene, modified by being extended from 1800 to 2890 oscillation frequencies, or near O; but at $\frac{1}{625}$ of a molecule all absorption practically ceases. (Plate IV.)

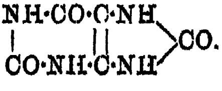
If we examine all the other azobenzene and azonaphthalene-derivatives, it is to be observed that the amplitude of the vibrations is virtually the same as in chrysoidine, and that the character of their curves is remarkably similar, though of course no two of them can be alike. The very varied constitution of the compounds as regards the hydrocarbon radicles from which they are derived, and their considerable number, 12, showing a great family likeness. renders the study of these curves of much interest, for it shows how much the nitrogen is concerned in the development of the colours, and how comparatively of small importance are the hydrocarbon radicles provided they are of the benzenoïd character. (Plates IV to XI.)

There are three curves besides the 12 referred to, which require some further notice. First, Tropæolin 000 No. 1, which is isomeric with Tropæolin 000 No. 2 (No. 1 contains α- and No. 2 β-naphthol), transmits all rays through $\frac{1}{125}$ of a molecule, while No. 2 absorbs all beyond 1780 oscillation frequencies, when only $\frac{1}{500}$ of a molecule is present. Next, there are two isomeric diazonaphthol-derivatives, "Acid Brown" and "Fast Red," the curves of which are very remarkable, though the one with all its differences seems to be a modification of the other. The singular fact about these colours is, that the difference between them in constitution is but slight, as will be perceived by the constitutional formulæ given :—

"Acid Brown." "Fast Red."

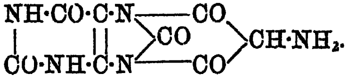
$$\overset{\alpha}{\mathrm{H}}\mathrm{SO_3{\cdot}C_{10}H_6{\cdot}}\underset{\alpha}{\mathrm{N}}:\underset{\alpha}{\mathrm{N}}\mathrm{{\cdot}C_{10}H_6{\cdot}}\underset{\alpha}{\mathrm{OH}} \qquad \overset{\alpha}{\mathrm{H}}\mathrm{SO_3{\cdot}C_{10}H_6{\cdot}}\underset{\alpha}{\mathrm{N}}:\underset{\alpha}{\mathrm{N}}\mathrm{{\cdot}C_{10}H_6{\cdot}}\underset{\beta}{\mathrm{OH}}.$$

Murexide was studied as being almost the only organic colouring matter of known constitution which is not derived from one of the hydrocarbon nuclei of the benzene class. The colour is due to the close combination of nitrogen- and carbon-atoms. It is easily derived from uric acid; it was therefore deemed advisable to examine this compound. Uric acid exhibits an extraordinary absorption-band when an aqueous solution of the acid is examined in layers 15 mm. in thickness. As the substance requires 15,000 parts of water for its solution, this is some indication of the extraordinary absorptive power of uric acid, and of the effect of the linking of several carbon- and nitrogen-atoms, and the combination of oxygen-atoms with the carbon. Urea, be it remembered, is extraordinarily diactinic. We have unfortunately no indisputable evidence of the constitution of uric acid and murexide, though the latest results obtained by E. Fischer appear to establish the formula of Medicus, which is the following (*Ber.*, **17**, 1776, and *Chem. Soc. J.*, 1884 (Abstracts), 1310) :—



It appears to be established that there is a carbamido-group containing two imido-groups, distinct from the nucleus, which is removed as alloxan on oxidation in an acid solution.

From the above formula, it is possible murexide may have the following constitution:—



One fact is established by this work, namely, that when absorption takes place in the visible region, the ultra-violet rays are also absorbed.

It appears hopeless to expect a strongly coloured substance to transmit the ultra-violet rays. The researches of H. C. Vogel, Eder, and of V. Schumann have given rise to an important extension of photography in the direction of preparing stained films sensitive to the less refrangible rays, and thereby capable of rendering the true relative values of different colours in black and white; it is therefore of interest to know the exact behaviour of various dyes towards all luminous and non-luminous vibrations.

When benzene in a molecule of a dye is replaced by xylene or cumene, it is a fact already recognised by chemists that the colour is altered by the transmitted rays being of less refrangibility the higher the homologue introduced.

On carefully comparing the curves of the rosaniline series of dyes, triphenylmethane and benzene, it is seen that they are modifications of the benzene curve, but the closeness of relationship of the triphenylmethane curve to the dyes is much greater than that of the benzene curve, and the curves of the three dyes are modified in such a manner that they follow each other closely. The modification is such that the molecules of greatest mass transmit least light, and the light is composed of rays vibrating with least rapidity, thus indicating a greater amplitude and less rapidity of vibration of the molecule.

The same remark applies to the diazo-colours; they all present curves which are modifications of the azobenzene curve.

In a paper "On Homologous Spectra" (*Chem. Soc. J.*, 1883, **43**, 390) which deals with the author's examination of the simple spark spectra of well-defined series of metallic elements, it is shown that there is a considerable evidence in support of the view that elements whose atomic weights differ by a constant quantity, and whose chemical character is similar, are truly homologous, that is to say, similarly constituted bodies, or in other words, they are the same kind of matter in different states of condensation. The emission spectra show that these elements are vibrating in the same manner, but at different rates, the rate of vibration depending upon the mass of the atom, the atoms of greatest mass having the slowest rate of vibration. This is in accord with what we know of the absorption spectra of homologous series of carbon compounds.

I desire to express my thanks to Professor Schorlemmer, F.R.S., for the specimen of aurin of perfect purity, to Messrs. Williams Brothers, and Ekin, and Professor Meldola, F.R.S., for other pure substances used in this investigation.

The examination of the dyes has been systematically carried out by Mr. W. R. Barnett, after a preliminary series of observations and drawings had been made by myself.

TRIPHENYLMETHANE. 0·244 gram in 20 c.c. alcohol. Molecular weight = 244. $CH(C_6H_5)_3$.

Thickness of layer of liquid........	10 mm.		9 mm.		8 mm.		7 mm.		6 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Continuous spectrum to.........	252	398	252	398	252	398	252	398	252	398
(a) Absorption band from........	—	—	—	—	252 to 329	398 to 303	252 to 329	398 to 303	252 to 329	398 to 303
Spectrum extends to.....	—	—	—	—	332	300	336	297	348	286
Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Continuous spectrum to........	253	395	254	394	254	394	254	394	256	390
(a) Absorption band from	253 to 329	395 to 303	254 to 315	394 to 317	254 to 315	394 to 317	254 to 315	394 to 317	256 to 298	390 to 334
Spectrum extends to.....	356	280	356	280	356	280	364	274	364	274

TRIPHENYLMETHANE. 0·244 gram in 100 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.
Continuous spectrum to	257	389	257	389			364	274	370	270
(*a*) Absorption band from.... ..	257 to 298	389 to 334	257 to 268	389 to 373	Same as 4 mm.		—	—	—	—
Spectrum extends to.....	364	274	364	274			—	—	376	265

TRIPHENYLMETHANE. 0·244 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Continuous spectrum to.........	370	270	376	265	382	261	382	261	382	261
(*b*) Absorption band from......	—	—	—	—	382 to 433	261 to 231	382 to 431	261 to 231	382 to 413	261 to 242
Spectrum extends to...	376	265	382	261	—	—	433	231	437	228

TRIPHENYLMETHANE. 0·244 gram in 2500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Continuous spectrum to.........	382	261	389	256					—	—
(*b*) Absorption band from........	382 to 411	261 to 243	389 to 403	256 to 247	Same as	4 mm.	Same as	3 mm.	—	—
Spectrum extends to.....	437	228	443	225					456	219

ROSANILINE BASE. 0·301 gram in 100 c.c.

Thickness of layer of liquid	20 mm.		10 mm.		5 mm.		4 mm.		3 mm.	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	153	650	166	600	166	600	166	600	166	600
Absorption band from	—	—	—	—	166 to 244	600 to 410	166 to 235	600 to 425	166 to 235	600 to 425
Rays transmitted to	—	—	—	—	263	350	277	361	306	326

ROSANILINE BASE—*continued*. 0·301 in 100 c.c.

Thickness of layer of liquid	2 mm.		1 mm.							
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	—	—	—	—	—	—
And extends to	166	600	166	600	—	—	—	—	—	—
Absorption band from	166 to 225	600 to 441	166 to 225	600 to 441	—	—	—	—	—	—
Rays transmitted to	315	317	315	317	—	—	—	—	—	—

ROSANILINE BASE. 0·301 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to.....	166	600	166	600	169	591	170	586	172	580
Absorption band from...........	166 to 225	600 to 441	166 to 225	600 to 441	169 to 225	591 to 441	170 to 225	586 to 441	172 to 221	580 to 452
Rays transmitted to.	315	317	315	317	325	307	330	302	332	300
Absorption band from...........	—	—	—	—	—	—	—	—	332 to 364	300 to 274
Rays transmitted to.	—	—	—	—	—	—	—	—	370	269

Rosaniline Base. 0·301 gram in 2500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to.....	172	580	172	580	172	580	574	174	177	562
Absorption band from	172 to 221	580 to 452	172 to 216	580 to 462	172 to 209	580 to 478	174 to 206	574 to 484	177 to 193	562 to 516
Rays transmitted to	332	300	332	300	335	298	443	225	443	225
Absorption band from	332 to 364	300 to 274	332 to 353	300 to 283	335 to 349	298 to 286	—	—	—	—
Rays transmitted to	370	269	403	247	414	241	—	—	—	—
Absorption band from	—	—	403 to 433	247 to 231	414 to 432	241 to 231	—	—	—	—
Rays transmitted at	—	—	433	231	443	225	—	—	—	—

Rosaniline Base. 0·301 gram in 12,500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at ..	139	719	139	719	139	719	139	719	139	719
And extends to	177	562	177	562	466	214	466	214	466	214
Absorption band from	177 to 193	562 to 516	177 to 188	562 to 530	—	—	—	—	—	—
Rays transmitted to	443	225	466	214	—	—	—	—	—	—

AURIN. 0·290 gram in 100 c.c.

Thickness of layer of liquid…….	60 mm.		30, 20, 15, and 10 mm		5 mm.		4 mm.		3 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to ….	153	650	166	600	177	562	177	562	181	550
Absorption band from ………..	barely measurable		—	—	—	—	177 to 306	562 to 326	181 to 304	550 to 328
Rays transmitted to.	—	—	—	—	—	—	315	317	315	317
Thickness of layer of liquid…….	2 mm.		1 mm.							
Spectrum begins at .	139	719	139	719	—	—	—	—	—	—
And extends to ….	183	545	188	530	—	—	—	—	—	—
Absorption band from ………..	183 to 297	545 to 336	188 to 288	530 to 346	—	—	—	—	—	—
Rays transmitted to.	325	307	335	298	—	—	—	—	—	—

AURIN. 0·290 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	188	530	192	520	193	516	195	511	198	504
Absorption band from	188 to 288	530 to 346	192 to 277	520 to 361	193 to 277	516 to 361	195 to 247	511 to 405	198 to 225	504 to 441
Rays transmitted to	335	298	343	290	349	286	364	274	414	241
Absorption band from............	—	—	—	—	349 to 389	286 to 256	364 to 389	274 to 256	—	—
Rays transmitted at.	—	—	—	—	389	256	389	256	—	—

AURIN. 0 290 gram in 2500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	198	504	202	494	206	484	433	231	466	214
Absorption band from	198 to 225	504 to 441	202 to 225	494 to 441	206 to 213	484 to 467	—	—	—	—
Rays transmitted to	414	241	414	241	414	241	—	—	—	—

ROSANILINE HYDROCHLORIDE. 0·3375 gram in 100 c.c. alcohol. $C_{20}H_{20}N_3Cl$.

Thickness of layer of liquid........	20 mm.		15 mm.		10 mm.		5 mm.		4 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	149	669	151	660	153	650	157	636	159	628
Thickness of layer of liquid........	3 n.m.		2 mm.		1 mm.					
Spectrum begins at .	139	719	139	719	139	719	—	—	—	—
And extends to	160	624	161	619	162	614	—	—	—	—
(*a*) Absorption band from........	160 to 250	624 to 399	161 to 247	619 to 405	162 to 244	614 to 410	—	—	—	—
Rays transmitted to........	277	361	277	361	299	334	—	—	—	—

ROSANILINE HYDROCHLORIDE. 0·3375 gram in 500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	162	614	166	600	166	600	167	598	169	591
(*a*) Absorption band from	162 to 244	614 to 410	166 to 236	600 to 423	166 to 236	600 to 423	167 to 226	598 to 440	169 to 219	591 to 456
Rays transmitted to	299	334	315	317	315	317	315	317	322	310
(*b*) Absorption band from	—	—	—	—	—	—	—	—	322 to 364	310 to 274
Rays transmitted to	—	—	—	—	—	—	—	—	403	247

ROSANILINE HYDROCHLORIDE. 0·3375 gram in 2500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	169	591	169	589	171	584	172	580	174	574
(*a*) Absorption band from	169 to 219	591 to 456	169 to 211	589 to 472	171 to 209	584 to 478	172 to 207	580 to 481	174 to 205	574 to 487
Rays transmitted to	322	310	329	303	332	300	332	300	442	225
(*b*) Absorption band from	322 to 364	310 to 274	329 to 364	303 to 274	332 to 349	300 to 286	332 to 349	300 to 286	—	—
Rays transmitted to	403	247	403	247	433	231	433	231	—	—

ROSANILINE HYDROCHLORIDE. 0·3375 gram in 12,500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	174	574	174	572	177	562	177	562	456	219
(*a*) Absorption band from	174 to 205	574 to 457	174 to 200	572 to 499	177 to 185	562 to 540	177 to 185	562 to 549	—	—
Rays transmitted to	442	225	442	225	442	225	456	219	—	—

HOFMANN'S VIOLET. 0·416 gram in 100 c.c. alcohol. $C_{20}H_{16}(CH_3)_3N,2HCl$.

Thickness of layer of liquid	25 mm.		20 mm.		15 mm.		10 mm.		5 mm.	
Rays transmitted very faint, too indistinct to measure	139	719	—	—	—	—	—	—	—	—
Spectrum begins at	—	—	139	719	139	719	Same	as last.	139	719
And extends to	—	—	145	686	147	680	—	—	149	670
(*a*) Absorption band from	—	—	—	—	—	—	—	—	149 to 250	670 to 399
Rays transmitted at	—	—	—	—	—	—	—	—	250	399

HOFMANN'S VIOLET. 0·416 gram in 100 c.c. alcohol—*continued.*

Thickness of layer of liquid........	4 mm.		3 mm.		2 mm.		1 mm.			
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	—	—
And extends to	149	666	150	664	151	660	153	650	—	—
(*a*) Absorption band from	149 to 235	666 to 425	150 to 225	664 to 441	151 to 225	660 to 441	153 to 214	650 to 467	—	—
Rays transmitted to	255	391	262	381	262	381	289	345	—	—

HOFMANN'S VIOLET. 0·416 gram in 500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	153	650	156	639	157	634	158	632	160	624
(*a*) Absorption band from........	153 to 214	650 to 467	156 to 210	639 to 474	157 to 202	634 to 493	158 to 201	632 to 497	160 to 193	624 to 504
Rays transmitted to......	289	345	308	324	308	324	315	317	315	317
(*b*) Absorption band from........	—	—	308 to 364	324 to 274	308 to 364	324 to 274	315 to 364	317 to 274	315 to 350	317 to 285
Rays transmitted at	—	—	364	274	370	269	370	269	389	256
(*c*) Absorption band from	—	—	—	—	—	—	370 to 433	269 to 231	389 to 431	256 to 231
Rays transmitted to	—	—	—	—	—	—	—	—	442	225

Hofmann's Violet. 0·416 gram in 2500 c c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	160	624	161	619	162	616	163	613	166	600
(*a*) Absorption band from........	160 to 198	624 to 504	161 to 193	619 to 516	162 to 192	616 to 515	163 to 185	613 to 530	166 to 185	600 to 539
Rays transmitted to........	315	317	322	310	393	253	442	225	442	225
(*b*) Absorption band from........	315 to 350	317 to 285	322 to 348	310 to 287	—	—	—	—	—	—
Rays transmitted to	389	256	389	256	—	—	—	—	—	—
(*c*) Absorption band from	389 to 431	256 to 231	389 to 411	256 to 243	393 to 411	253 to 243	—	—	—	—
Rays transmitted to.......	442	225	442	225	442	225	—	—	—	—

HOFMANN'S VIOLET. 0·416 gram in 12,500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	Continuous spectrum with mere trace of band (a).			
And extends to	166	600	166	600	168	598				
(a) Absorption band from	166 to 185	600 to 539	166 to 181	600 to 550	168 to 174	598 to 574				
Rays transmitted to	442	225	442	225	442	225				

IODINE GREEN. 0·627 gram in 100 c.c. water. $C_{20}H_{16}(CH_3)_3N_3,2CH_3I$.

Thickness of layer of liquid	20, 15, 10 mm.		5 mm.		4 mm.		3 mm.		2 mm.	
Spectrum begins at.	No spectrum transmitted.		133	749	133	749	133	749	133	749
And extends to			139	719	139	719	139	719	139	719
(a) Absorption band from........			139 to 203	719 to 490	139 to 202	719 to 494	139 to 195	719 to 512	139 to 191	719 to 522
Rays transmitted to			219	455	219	455	219	455	225	441
(b) Absorption band from........			219 to 277	455 to 361	219 to 277	455 to 361	219 to 271	455 to 368	225 to 263	441 to 380
Rays transmitted to......			289	345	289	345	297	336	304	328

IODINE GREEN. 0·672 gram in 500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	133	749	133	749	133	749	133	749	133	749
And extends to	144	694	147	680	148	675	149	669	151	660
(*a*) Absorption band from	144 to 183	694 to 545	147 to 176	680 to 568	148 to 174	675 to 572	149 to 170	669 to 586	151 to 161	660 to 620
Rays transmitted to	230	434	315	317	389	256	394	253	456	219
(*b*) Absorption band from........	230 to 244	434 to 410	—	—	—	—	—	—	—	—
Rays transmitted to	308	324	—	—	—	—	—	—	—	—
(*c*) Absorption band from........	308 to 349	324 to 286	315 to 349	317 to 286	—	—	—	—	—	—
Rays transmitted to	364	274	389	256	—	—	—	—	—	—
(*d*) Absorption band from	This description is the same as for 1 mm of the previous solution.		389 to 425	256 to 235	389 to 414	256 to 241	394 to 414	253 to 241	—	—
Rays transmitted to			442	225	442	225	442	225	—	—

IODINE GREEN. 0·627 gram in 2500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	133	749	133	749	133	749	133	749	133	749
And extends to	151	660	153	650	Faint trace of Absorption band (a) too indistinct to measure.		—	—	—	—
(a) Absorption band from........	151 to 161	660 to 620	153 to 160	650 to 624			—	—	—	—
Rays transmitted to	456	219	466	214	466	214	466	214	466	214

AZOBENZENE. 0·182 gram in 100 c.c. alcohol.

Thickness of layer of liquid	60 mm.		50 mm.		40 mm.		30 mm.		20 mm.	
Spectrum begins at . And extends to	139 162	719 616	Same as	60 mm.	139 186	719 537	139 188	719 530	139 192	719 518
Thickness of layer of liquid	15 mm.		10 mm.							
Spectrum begins at . And extends to	139 193	719 516	139 196	719 509	— —	— —	— —	— —	— —	— —

AZOBENZENE. 0·182 gram in 100 c.c. alcohol—*continued.*

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	Same as	3 mm.	139	719
And extends to	202	494	206	484	208	479			277	361
Absorption band from..	202 to 264	494 to 378	206 to 247	484 to 405	208 to 247	479 to 405			—	—
Rays transmitted to.	272	367	275	363	277	361			—	—

AZOBENZENE. 0·182 gram in 500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	277	361	250	357	280	357	280	357	293	341
Absorption band from	—	—	280 to 339	357 to 256	280 to 383	357 to 260	280 to 364	357 to 274	293 to 349	341 to 286
Rays transmitted to.	—	—	—	—	389	256	392	254	413	241

AZOBENZENE. 0·182 gram in 2500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	Same as	3 mm.	139	719
And extends to	293	341	306	326	315	317			466	214
Absorption band from............	293 to 349	341 to 286	306 to 329	326 to 303	315 to 329	317 to 303			—	—
Rays transmitted to.	413	241	442	225	466	214			—	—

CHRYSOIDINE. Diamidoazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_3(NH_2)_2$. 0·212 gram in 100 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	171	534	173	577	174	572	179	536	181	550
Absorption band from	—	—	—	—	—	—	—	—	181 to 238	550 to 346

Chrysoidine. 0·212 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	181	550	185	540	188	530	190	525	193	516
Absorption band from	181 to 288	550 to 346	185 to 277	540 to 361	188 to 272	530 to 367	190 to 268	525 to 373	193 to 255	516 to 385
Rays transmitted to	—	—	308	324	364	274	364	274	389	256

Chrysoidine. 0·212 gram in 2500 c c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	193	516	198	504	199	500	202	494	465	215
Absorption band from	193 to 255	516 to 385	198 to 247	504 to 405	199 to 206	500 to 422	202 to 227	494 to 439	—	—
Rays transmitted to	389	256	389	256	403	247	465	214	—	—
Absorption band from	—	—	389 to 431	256 to 232	403 to 429	247 to 232	—	—	—	—
Rays transmitted to	—	—	441	226	455	219	—	—	—	—

BISMARCK BROWN. 0·227 in 100 c.c. of water.

Thickness of layer of liquid........	25 mm., 15 mm.		10 mm.		5 mm.		4 mm.		3 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	153 very	650 faint.	166	601	166	600	170	586	174	574
Thickness of layer of liquid........	2 mm.		1 mm.							
Spectrum begins at .	139	719	139	719	—	—	—	—	—	—
And extends to	179	556	185	540	—	—	—	—	—	—
Absorption band from	179 to 288	556 to 346	185 to 277	540 to 361	—	—	—	—	—	—
Rays transmitted to	300	332	364	274	—	—	—	—	—	—

BISMARCK BROWN. 0·227 in 500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	185	540	194	514	202	493	206	484	214	467
Absorption band from	185 to 277	540 to 361	194 to 263	514 to 380	202 to 263	493 to 380	206 to 251	484 to 398	214 to 246	467 to 407
Rays transmitted to	364	274	389	256	389	256	433	231	442	226

BISMARCK BROWN. 0·227 gram in 2500 c c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	214	467	—	—	—	—	—	—	—	—
Absorption band from	214 to 246	467 to 407	—	—	—	—	—	—	—	—
Rays transmitted to	442	226	456	219	456	219	466	214	466	214

TROPÆOLIN O. 0·1 gram in 100 c.c.

Thickness of layer of liquid........	50 mm. and 30 mm.		15 mm.		5 mm.		4 mm.		3 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	166	600	177	562	188	530	193	516	198	504
Absorption band from...........	60 mm. cut off all the spectrum.		—	—	188 to 364	530 to 274	193 to 349	516 to 286	198 to 348	504 to 287
Rays transmitted at			—	—	364	274	364	274	364	274
Thickness of layer of liquid........	2 mm.		1 mm.							
Spectrum begins at.	139	719	139	719	—	—	—	—	—	—
And extends to	202	494	210	475	—	—	—	—	—	—
Absorption band from	202 to 329	494 to 308	210 to 308	475 to 329	—	—	—	—	—	—
Rays transmitted at	369	270	389	256	—	—	—	—	—	—

TROPÆOLIN O. 0·1 gram in 500 c c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	210	475	210	475	214	467	217	459	457	218
Absorption band from	210 to 303	475 to 329	210 to 277	475 to 361	214 to 263	467 to 380	217 to 263	459 to 380	—	—
Rays transmitted at	389	256	442	226	442	226	442	226	—	—

TROPÆOLIN O. 0·1 gram in 2500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at.	139	719	139	719	same	as last.	same	as last.	same	as last.
And extends to.....	457	218	466	214	—	—	—	—	—	—

TROPÆOLIN 000. No. 1. 0·324 gram in 500 c.c.

Thickness of layer of liquid	50 mm.		25 mm.		20 mm. and 15 mm.		10 mm.		5 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	Same as	last but	139	719	139	719	139	719
And extends to	166	600	much	stronger	172	580	174	574	177	562
Absorption band from	—	—	—	—	—	—	—	—	177 to 263	562 to 380
Rays transmitted to.	—	—	—	—	—	—	—	—	288	346
Thickness of layer of liquid	4 mm.		3 mm.		2 mm.		1 mm.			
Spectrum begins at .	139	719	139	719	139	719	139	719	—	—
And extends to	183	545	188	530	188	530	193	516	—	—
Absorption band from	183 to 263	545 to 380	188 to 244	530 to 410	188 to 244	530 to 410	193 to 235	516 to 425	—	—
Rays transmitted to.	306	326	315	317	389	256	442	226	—	—

TROPÆOLIN 000. No. 1. 0·324 gram in 2500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	193	516	202	494	214	467	224	444	466	214
Absorption band from	193 to 235	516 to 425	202 to 225	494 to 441	214 to 225	467 to 441	224 to 225	444 to 441	—	—
Rays transmitted to.	442	226	442	226	442	226	457	218	—	—

TROPÆOLIN 000. No. 2. 0·1 gram in 100 c.c.

Thickness of layer of liquid	60 mm. and 50 mm.		15 mm.		5 mm.		4 mm.		3 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	166	600	172	580	177	562	177	562	181	550
Absorption band from	Very faint, barely measurable.		—	—	—	—	177 to 277	562 to 361	181 to 277	550 to 361
Rays transmitted to			—	—	—	—	294	340	300	332

TROPÆOLIN 000. No. 2. 0·1 gram in 100 c.c.—*continued*.

Thickness of layer of liquid	2 mm.		1 mm.							
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	—	—	—	—	—	—
And extends to	181	550	188	530	—	—	—	—	—	—
Absorption band from	181 to 277	550 to 361	188 to 263	530 to 380	—	—	—	—	—	—
Rays transmitted to.	306	326	364	274	—	—	—	—	—	—

TROPÆOLIN 000. No. 2. 0·1 in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	188	530	188	530	193	516	198	504	438	228
Absorption band from	188 to 263	530 to 380	188 to 250	530 to 399	193 to 236	516 to 423	198 to 225	504 to 441	—	—
Rays transmitted to.	364	274	364	274	389	256	414	241	—	—

TROPÆOLIN 000. No. 2. 0·1 gram in 2500 c.c.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	Same	as last.	Same	as last.
And extends to	438	228	457	218	466	214				

CUMENE-AZO-β-NAPHTHOLDISULPHONIC ACID. Molecular weight = 494. $C_9H_{11}\cdot N : N\cdot C_{10}H_4(HSO_3)_2\cdot OH\beta$(Na Salt). 49·4 mgrms. in 100 c c. OH_2.

Thickness of layer of liquid........	60 mm.		20 mm.		15 mm.		10 mm.		9 mm.	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	164	608	168	595	168	595	169	589	170	586
Thickness of layer of liquid........	**8 mm.**		**7 mm.**		**6 mm.**		**5 mm.**		**4 mm.**	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	171	583	171	581	173	577	174	574	176	568
Absorption band from...........	171 to 264	583 to 378	171 to 264	581 to 378	173 to 264	577 to 378	174 to 264	574 to 378	176 to 225	568 to 441
Rays transmitted to	—	—	277	361	277	361	277	361	329	303

CUMENE-AZO-β-NAPHTHOLDISULPHONIC ACID. Molecular weight = 494. $C_9H_{11}\cdot N:N\cdot C_{10}H_4(HSO_3)_2\cdot OH\beta$ (Na Salt). 49·4 mgrms. in 100 c.c. OH_2—*continued.*

Thickness of layer of liquid	3 mm.		2 mm.		1 mm.					
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	—	—	—	—
And extends to	177	564	181	549	433	230	—	—	—	—
Absorption band from	177 to 225	564 to 441	181 to 219	549 to 445	—	—	—	—	—	—
Rays transmitted to.	364	274	364	274	—	—	—	—	—	—

$HSO_3\cdot C_8H_8\cdot N:N\cdot C_{10}H_4(HSO_3)_2\cdot OH\beta$(Na Salt). Molecular weight = 578. 57·8 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 mm.		25 mm.		20 mm.		15 mm.		10 mm.	
Spectrum begins at .	139	719	139	719	Same	as last.	Same	as last.	139	719
And extends to	174	574	176	568					177	562

$HSO_3 \cdot C_6H_3 \cdot N : N \cdot C_{10}H_4(HSO_3)_2 \cdot OH\beta$ (Na Salt). Molecular weight = 578. 57·8 mgrms. in 100 c.c. OH_2—*continued.*

Thickness of layer of liquid	9 mm.		8 mm.		7 mm.		6 mm.		5 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	179	558	179	557	180	555	180	553	182	549
Absorption band from	—	—	179 to 278	557 to 360	180 to 278	555 to 360	180 to 261	553 to 382	182 to 228	549 to 437
Rays transmitted to.	—	—	—	—	288	346	288	346	294	340
Thickness of layer of liquid	4 mm.		3 mm.		2 mm.		1 mm.			
Spectrum begins at .	139	719	139	719	139	719	139	719	—	—
And extends to	183	544	184	542	186	537	389	256	—	—
Absorption band from	183 to 228	544 to 437	184 to 226	542 to 441	186 to 214	537 to 467	—	—	—	—
Rays transmitted to.	333	300	364	274	370	270	—	—	—	—

AMIDO-AZO-α-NAPHTHALENE, $C_{10}H_7\cdot\underset{\alpha}{N}:\underset{\alpha}{N}\cdot C_{10}\underset{\alpha}{H_6}\cdot NH_2$. Molecular weight = 297. 29·7 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid........	60 mm.		20 mm.		15 mm.		10 mm.		5 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	160	624	169	591	171	584	172	580	181	550
Absorption band from	—	—	—	—	—	—	—	—	181 to 271	550 to 368
Rays transmitted to	—	—	—	—	—	—	—	—	278	361
Thickness of layer of liquid........	4 mm.		3 mm.		2 mm.		1 mm.			
Spectrum begins at	139	719	139	719	139	719	139	719	—	—
And extends to	183	545	185	539	190	524	198	504	—	—
Absorption band from	183 to 263	545 to 330	185 to 263	539 to 380	190 to 247	524 to 405	198 to 236	504 to 423	—	—
Rays transmitted to	315	317	315	317	333	300	364	274	—	—

AMIDO-AZO-α-NAPHTHALENE 29·7 mgrms. in 500 c c OH_2.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at	139	719	139	719	139	719	—	—	—	—
And extends to	198	504	203	490	210	476	—	—	—	—
Absorption band from	198 to 236	504 to 423	203 to 230	490 to 434	210 to 220	476 to 454	—	—	—	—
Rays transmitted to	364	274	—	—	—	—	—	—	—	—

AMIDO-AZO-β-NAPHTHALENE. $\underset{\beta}{C_{10}H_7}\cdot\underset{\alpha}{N:N}\cdot\underset{\beta}{C_{10}H_6\cdot NH_2}$. Molecular weight = 297. 29·7 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 mm.		20 mm.		15 mm.		10 mm.		5 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	172	580	181	551	183	545	185	540	192	520
Thickness of layer of liquid	4 mm.		3 mm.		2 mm.		1 mm.			
Spectrum begins at.	139	719	139	719	139	719	139	719	—	—
And extends to	194	514	196	510	200	500	203	492	—	—
Absorption band from	—	—	196 to 247	510 to 405	200 to 228	500 to 437	203 to 225	492 to 441	—	—
Rays transmitted to.	—	—	272	367	330	302	343	283	—	—

AMIDO ·β-NAPHTHALENE 29·7 mg 500 c.c.

	5 m						2 mm.
Spectrum begins at.		719	139	719		719	
And extends to .. .		492	209	478		456	
Absorption band from	3 to 5	492 to 44		478 448	218		
Rays tr	343	283					

HELIANTHIN Molecular weight = 305. (A free acid.) $\mathrm{HSO_3\cdot C_6H_4\cdot \underset{(4)}{N}:\underset{(4)}{N}\cdot C_6H_4\cdot \underset{(1)}{N}(CH_3)_2}$. 30 5 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 mm.		20 mm.		15 mm		10 mm.		9 mm	
Description of spectrum	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	173	577	176	568	180	555	181	551	183	546
Absorption band from	—	—	—	—	—	—	181 to 288	551 to 346	183 to 288	546 to 346
Rays transmitted to	—	—	—	—	—	—	300	333	301	331
Thickness of layer of liquid	8 mm		7 mm.		6 mm		5 mm.		4 mm.	
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to ...	184	543	185	540	186	537	186	536	194	514
Absorption band from	184 to 288	543 to 346	185 to 277	540 to 361	186 to 277	537 to 361	186 to 277	536 to 361	194 to 277	514 to 361
Rays transmitted to	308	324	315	317	315	317	332	300	364	274
Absorption band from	—	—	—	—	—	—	332 to 433	300 to 231	364 to 389	274 to 256
Rays transmitted to	—	—	—	—	—	—	—	—	442	225

HELIANTHIN. Molecular weight = 305. (A free acid.) $\mathrm{HSO_3 \cdot C_6H_4 \cdot \underset{(4)}{N} : \underset{(4)}{N} \cdot C_6H_4 \cdot \underset{(1)}{N}(CH_3)_2}$.

30·5 mgrms. in 100 c.c. OH_2—*continued.*

Thickness of layer of liquid	3 mm.		2 mm.		1 mm.					
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	—	—	—	—
And extends to	196	509	199	501	203	492	—	—	—	—
Absorption band from	196 to 277	509 to 361	199 to 263	501 to 380	203 to 250	492 to 399	—	—	—	—
Rays transmitted to.	370	270	466	214	466	214	—	—	—	—
Absorption band from	370 to 389	270 to 256	—	—	—	—	—	—	—	—
Rays transmitted to	442	225	—	—	—	—	—	—	—	—

HELIANTHIN. 30·5 mgrms. in 500 c.c. OH_2.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm	
Spectrum begins at.	139	719	139	719			139	719		
And extends to	203	492	218	458	Same	as last	446	214	Same	as last.
Absorption band from	203 to 250	492 to 399	218 to 246	458 to 407			—	—		
Rays transmitted to.	466	214	466	214			—	—		

Biebrich Scarlet. Molecular weight = 557 (Na salt). $HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4(HSO_3) \cdot N_2 \cdot C_{10}H_6OH$. 55·7 mgrms. in 100 c.c. OH_2. β

Thickness of layer of liquid	60 mm		50, 40, 30 mm.		20 mm		15 mm		10 mm.	
Description of spectrum	$\frac{1}{\lambda}$	λ	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.
Spectrum begins at. And extends to	139 166	719 600	Same as	60 mm.	139 168	719 592	139 170	719 588	139 174	719 574
Thickness of layer of liquid	5 mm		4 mm		3 mm		2 mm		1 mm	
Spectrum begins at And extends to ... Absorption band from	139 180 180 to 247	719 553 553 to 406	139 186 186 to 228	719 535 535 to 438	139 192 192 to 228	719 518 518 to 438	139 369 —	719 270 —	139 388 —	719 257 —

CROCEINE SCARLET. Molecular weight = 454. $C_6H_5{\cdot}N{:}N{\cdot}\underset{(1)}{C_6H_4}{\cdot}\underset{(4)}{N}{:}N{\cdot}\underset{\alpha}{C_{10}}H_5{\cdot}\underset{\alpha}{(HSO_3)}{\cdot}\underset{\beta}{OH}$ (Na salt). 45·4 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 mm.		50, 40, 30, and 20 mm		15 mm.		10 mm.		9 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	Same as	60 mm.	139	719	139	719	139	719
And extends to	166	600			167	596	172	580	173	577
Absorption band from	—	—	—	—	—	—	172 to 358	580 to 288	173 to 350	577 to 285
Rays transmitted to.	—	—	—	—	—	—	—	—	353	283
Thickness of layer of liquid	8 mm.		7 mm.		6 mm.		5 mm		4 mm	
Spectrum begins at.	139	719	139	719	139	719	139	719	139	719
And extends to	174	574	174	571	176	568	177	564	179	557
Absorption band from...........	174 to 350	574 to 285	174 to 315	571 to 317	176 to 315	568 to 317	177 to 228	564 to 438	179 to 228	557 to 438
Rays transmitted to.	353	283	364	274	364	274	364	274	369	270
Thickness of layer of liquid	3 mm.		2 mm.		1 mm.					
Spectrum begins at	139	719	139	719	139	719	—	—	—	—
And extends to	180	553	192	520	389	256	—	—	—	—
Absorption band from	180 to 222	553 to 450	192 to 208	520 to 479	—	—	—	—	—	—
Rays transmitted to.	389	256	389	256	—	—	—	—	—	—

BENZENE-AZO-β-NAPHTHOLSULPHONIC ACID. Molecular weight = 452. $C_6H_5{\cdot}N{:}N{\cdot}C_{10}H_4(HSO_3)_2{\cdot}\underset{\beta}{OH}$ (Na salt).

45·2 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid........	60 mm.		20 mm.		15 mm.		10 mm.		5 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	162	816	166	600	168	592	169	589	181	550
Absorption band from	—	—	—	—	—	—	—	—	181 to 272	550 to 367
Rays transmitted to.	—	—	—	—	—	—	—	—	289	346
Thickness of layer of liquid........	4 mm.		3 mm.		2 mm.		1 mm.			
Spectrum begins at.	139	719	139	719	139	719	139	719	—	—
And extends to	182	547	185	540	188	530	191	522	—	—
Absorption band from	182 to 268	547 to 373	185 to 236	540 to 423	188 to 228	530 to 438	191 to 225	522 to 441	—	—
Rays transmitted to.	299	334	306	326	384	274	389	256	—	—

DIAZO. No. 10. 45·2 mgrms. in 500 c.c. OH_2.

Thickness of layer of liquid........	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Spectrum begins at.	139	719	139	719	—	—	—	—	—	—
And extends to	191	522	195	512	—	—	—	—	—	—
Absorption band from	191 to 225	522 to 441	195 to 216	512 to 460	—	—	—	—	—	—
Rays transmitted to	339	256	—	—	—	—	—	—	—	—

FAST RED. Molecular weight = 400 (Na salt). $\overset{\alpha}{\mathrm{HSO_3}}\cdot\mathrm{C_{10}H_6}\cdot\underset{\alpha}{\mathrm{N}}:\underset{\alpha}{\mathrm{N}}\cdot\mathrm{C_{10}H_6}\cdot\underset{\beta}{\mathrm{OH}}$. 400 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 mm.		50 mm		40 mm		30 mm.		20 mm.	
Description of spectrum.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ	$\frac{1}{\lambda}$	λ	$\frac{1}{\lambda}$	λ	$\frac{1}{\lambda}$	λ.
Spectrum begins at .	139	719	Same as	60 mm.	139	719	Same as	40 mm.	139	719
And extends to	158	632			160	624			163	611
Thickness of layer of liquid	10 mm.		5 mm		4 mm		3 mm.		2 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	165	605	170	586	171	583	175	570	190	524
Absorption band from...........	—	—	170 to 263	586 to 380	171 to 247	583 to 405	175 to 247	570 to 405	190 to 227	524 to 439
Rays transmitted to.	—	—	283	346	306	326	329	303	370	270
Thickness of layer of liquid	1 mm									
Spectrum begins at .	139	719	—	—	—	—	—	—	—	—
And extends to ...	226	441	—	—	—	—	—	—	—	—
Absorption band from	226 to 227	441 to 439	—	—	—	—	—	—	—	—
Rays transmitted to	369	257	—	—	—	—	—	—	—	—

Acid Brown. Molecular weight = 400 (Na salt). $\overset{\alpha}{HSO_3}\cdot C_{10}H_6\cdot\underset{\alpha}{N}:\underset{\alpha}{N}\cdot C_{10}H_6\cdot\underset{\alpha}{OH}$. 400 mgrms. in 100 c.c. OH_2.

Thickness of layer of liquid	60 and 50 mm.		40 mm.		30 mm.		20 mm.		15 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	162	616	163	611	166	600	172	580	177	562
Thickness of layer of liquid	10 mm.		9 mm.		8 and 7 mm.		6 mm.		5 mm.	
Spectrum begins at	139	719	139	719	Same as	9 mm.	139	719	139	719
And extends to	195	512	221	451			288	346	308	324
Absorption band from	—	—	221 to 250	451 to 399			—	—	—	—
Rays transmitted to	—	—	277	361			—	—	—	—
Thickness of layer of liquid	4 mm		3 mm		2 mm		1 mm			
Spectrum begins at	139	719	139	719	139	719	139	719	—	—
And extends to	315	317	364	274	389	256	412	225	—	—

MUREXIDE. 0·283 gram in 100 c c. water.

Thickness of layer of liquid........	25 mm. and 15 mm.		10 mm.		5 mm.		4 mm.		3 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at.	No spectrum		139	719	139	719	139	719	139	719
And extends to....			153	650	160	624	160	624	160	624
Absorption band from...........			—	—	160 to 236	624 to 423	160 to 236	624 to 423	160 to 236	624 to 423
Rays transmitted to			—	—	253	395	254	394	254	393
Thickness of layer of liquid........	2 mm.		1 mm.							
Spectrum begins at.	139	719	139	719	—	—	—	—	—	—
And extends to....	166	600	170	586	—	—	—	—	—	—
Absorption band from...........	166 to 229	600 to 435	170 to 225	586 to 441	—	—	—	—	—	—
Rays transmitted to	257	389	261	382	—	—	—	—	—	—

MUREXIDE. 0·283 gram in 500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.		2 mm.		1 mm.	
Description of spectrum.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$.	λ.	$\frac{1}{\lambda}$	λ.	$\frac{1}{\lambda}$.	λ.
Spectrum begins at	139	719	139	719	139	719	139	719	139	719
And extends to	170	586	177	562	177	562	183	545	389	256
Absorption band from	170 to 225	586 to 441	177 to 225	562 to 411	177 to 209	562 to 478	183 to 206	515 to 484	389 to 433	256 to 231
Rays transmitted to	261	382	263	380	277	361	364	274	443	225
Absorption band from	—	—	263 to 329	380 to 303	377 to 329	361 to 303	361 to 434	274 to 230	—	—
Rays transmitted to	—	—	353	282	353	282	434	230	—	—

MUREXIDE. 0·283 gram in 2500 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm		2 mm.		1 mm.	
Spectrum begins at .	139	719	139	719	139	719	139	719	139	719
And extends to	389	256	456	219	456	219	456	219	466	214
Absorption band from	389 to 433	256 to 231	—	—	—	—	—	—	—	—
Rays transmitted to	443	225	—	—	—	—	—	—	—	—

Notes to the Plates.

The solar lines represented on the scale have the following values in oscillation frequencies and tenth-metrets of wave-length:—

	$\frac{1}{\lambda}$.	λ.		$\frac{1}{\lambda}$.	λ.
A....	1314	7604	M....	2683	3727
B....	1455	6867	N....	2793	3580
C ...	1523	6562	O....	2907	3440
D....	1696	5892	P....	2976	3360
E....	1897	5269	Q....	3044	3285
F....	2056	4860	R....	3145	3179
G....	2321	4307	S....	3225	3100
H....	2519	3967	T....	3311	3020
K....	2542	3933	U....	3396	2947
L....	2618	3820		—	—

In many of the diagrams the curves are interrupted between the extreme limit of the spectrum in the red and the next point at which absorption occurs; this means that with the greatest thickness of liquid all intermediate rays were transmitted. For instance, on Plate I, benzene transmits all rays between A 1314 and 3750, and triphenylmethane transmits all between A and K. Instances where the light is almost entirely absorbed are indicated by the curve being continued by a dotted line, as in rosaniline hydrochloride.

Plate I. It will be noted that the benzene curve is drawn to the same scale as the other curves on this plate.

Iodine green appeared to transmit more of the less refrangible red rays than the other rosaniline-derivatives. This may have been due to the colour being favourable to viewing this end of the spectrum, the more brilliant rays being absorbed and those which are feeble thus rendered visible. The following table explains the scales upon the diagrams. As often as possible, 1 milligram-molecule of a substance is dissolved in 20 c.c. and examined in thicknesses of from 1 mm. to 5 mm.; the solution, if too strong, is then diluted five times and again examined in the same way.

	Volume of liquid containing 1 milligram-molecule of substance.	Proportional thicknesses of liquid.	Proportional part of 1 milligram-molecule observed through 1 mm.
Original solution..	20 c.c.	1 to 5 mm.	$\frac{1}{5}$
1st Dilution ...	100	5 to 25	$\frac{1}{25}$
2nd „	500	25 to 125	$\frac{1}{125}$
3rd „	2,500	125 to 625	$\frac{1}{625}$
4th „	12,500	625 to 3125	$\frac{1}{3125}$

When two or more curves on one plate refer to solutions which, according to the notes, are of different strengths, the curve drawn from the strongest solution is reduced to the same dimensions as if drawn from the weakest.

In the case of two of the curves, Plate VI and No. 1 on Plate IX, exact molecular proportions were not taken for examination, and a correction has been made for this.

XXI.—*Some Silicon Compounds and their Derivatives.* I. *The Action of Silicon Tetrabromide on Thiocarbamide.*

By J. Emerson Reynolds, M.D., F.R.S., Professor of Chemistry,
University of Dublin.

Although a large number of silicon analogues of carbon compounds are known, it is remarkable that we do not find among them any well-defined representatives of cyanogen or its derivatives. This consideration led me some years ago to commence the investigation of reactions in which silicon and nitrogen take part. In the course of this work, a considerable number of new facts have been observed and reactions examined, especially those in which the silicon haloids and organic nitrogen compounds are concerned.

Several of the compounds obtained have been exhibited from time to time at meetings of the Royal Dublin Society, and those especially referred to in this communication were shown at the conversazione of the Royal Society in June last. These bodies were chiefly derived from compounds which include ammonia residues such as amines, amides, and amidic acids, thus the interesting work just published by Mr. Harden touches at one point (the action of a silicon chloride on aniline), that in which I have been engaged.

Early in the course of the general investigation, it was found that silicon tetrabromide is a more manageable reagent than the corresponding chloride. The former is much less volatile—boiling at 153°, the boiling point of the chloride being only 59°—and the bromide is not so rapidly decomposed by water.

Even with the bromide, some of the reactions above referred to are very complicated, particularly when oxygen is present; but the change which I propose to describe in the present paper is a tolerably simple one, and is that which takes place when silicon tetrabromide acts on thiocarbamide, a substance which I obtained in the course of a former research (*J. Chem. Soc.*, 1869, **22**, 1).

I. *The Action of Silicon Tetrabromide on Thiocarbamide.*

When pure dry thiocarbamide in very fine powder is gently warmed with a solution of silicon tetrabromide in crystallisable benzene* combination takes place slowly. At first the particles of thiocarbamide adhere, and after some time a slightly yellowish semi-fused mass is obtained, which becomes a thick liquid at the temperature of the boiling benzene.

The composition of the product—which like thiocarbamide itself is scarcely soluble in benzene—was found by successive analyses to vary with the length of time during which the mixture was heated. The products contained the elements of silicon tetrabromide and thiocarbamide, and the proportion of the former to the amide rose until the ratio was reached of—

$$SiBr_4 : 8(CSN_2H_4).$$

This ratio was not exceeded even when the amide was heated with a considerable excess of the bromide for several hours at the boiling point of the benzene mixture.

After several trials the following mode of operating was found to afford a satisfactory product when using comparatively large quantities of the materials.

100 grams of pure and perfectly dry thiocarbamide in very fine powder was added gradually and with frequent agitation to a mixture of 28 c.c. of silicon tetrabromide with 250 c.c. of crystallisable benzene contained in a flask. The volume of liquid is sufficient to form a thin cream when the powder is evenly diffused through it. The mixture, carefully protected from moisture, was allowed to stand over night, when slight action took place, and a partially coherent mass was obtained in the morning. The flask was now connected with a long reflux condenser, and heated on the water-bath nearly to the boiling point of benzene. The thiocarbamide became pasty† as combination proceeded, and could then be diffused through the hot liquid in droplets when the contents of the flask were agitated. Three hours' heating of the above quantities at the boiling point of benzene proved to be sufficient. At the end of the operation, the product subsided as a heavy, rather viscid mass, which gradually solidified on cooling.

The benzene poured off from the product had a somewhat alliaceous odour, and contained some silicon and bromine. The ratio of silicon to bromine in this residual solution was found to be—

---

* The benzene solution was found to act more regularly than the undiluted tetrabromide.

† The melting point of thiocarbamide is 149°, so that liquefaction in presence of tetrabromide of silicon takes place at a temperature 65° lower.

$$Si : Br_{4{\cdot}02};$$

therefore it contains the excess of tetrabromide left by the 100 grams of thiocarbamide, in addition to small quantities of secondary products. This residual benzene solution proved useful in future experiments.

The solid product obtained in such an operation was well washed with cold benzene, and then boiled with a fresh quantity for some time in order to remove excess of tetrabromide: when cold, it was rapidly broken up, again washed with benzene, and dried by a gentle heat: in all these operations, contact with moisture was carefully avoided.

The body which results from this treatment is, when freshly prepared, a somewhat translucent brittle substance without distinct crystalline structure. It is yellowish, and the colour deepens considerably on exposure to air owing to evident decomposition. It is readily decomposed by moisture, and gives off fumes of hydrobromic acid as well as a sulphuretted odour. It becomes pasty below 100°, but begins to decompose when the temperature is raised much above that point.

Good solvents of silicon tetrabromide, such as benzene, chloroform. carbon bisulphide, and ethyl bromide, failed to extract sensible quantities of silicon bromide from the compound in question. Thiocarbamide itself is not dissolved by any of the above-named liquids. On the other hand, solvents of thiocarbamide such as water and anhydrous alcohol, especially the latter, did not dissolve out the unchanged amide when the material was properly prepared, but the alcoholic solution contained derivatives of thiocarbamide and of silicon tetrabromide, which were in part due to the chemical action of the alcohol. These products will be again referred to. I may add that no solvent for the compound was found which did not at the same time obviously decompose it.

A portion of a freshly prepared specimen which had been very carefully washed with benzene, was dried and powdered for analysis. Care was taken to expose it as little as possible to the air during the treatment. It was found to contain the elements of thiocarbamide and of silicon bromide.

The following data were obtained:—

I. 1·022 grams of substance gave 0·242 gram of N, = 23·67 per cent. of N = 64·24 per cent. of CSN_2H_4.

II. 1·001 grams gave 0·0634 of SiO_2 = 2·95 per cent. of Si = 36·66 per cent. of $SiBr_4$.

And 1·96 gram $BaSO_4$ = 63·96 per cent. of CSN_2H_4.

	Theory.		Experiment.	
			I.	II.
$SiBr_4$	348	36·41	—	36·66
$8(CSN_2H_4)$	608	63·59	64·24	63·96

The results agree fairly with the formula—

$SiBr_4,8(CSN_2H_4)$.*

If this substance were a mixture of excess of thiocarbamide with a compound of the amide with silicon tetrabromide, it should be capable of taking up more of the bromide by continued action, but that was not found to be the case. Another preparation was made in which a larger excess of tetrabromide was used (as the fresh 27 c.c. of tetrabromide were dissolved in the benzene solution left from a former operation), and the mixture was finally heated to the boiling point of benzene for rather more than five and a half hours, or for nearly double the time given in the former operation. The product obtained was more yellowish and rather less translucent, but was found to contain a *less* proportion of silicon tetrabromide than before. In order to trace the cause of this difference, a more detailed analysis of the product was made than seemed necessary in the former case.

The following data were obtained :—

I. 1·312 grams gave 0·0716 SiO_2 and 2·4128 $BaSO_4$.
II. 1·0012 „ 1·8706 $BaSO_4$.
III. 0·8099 „ 0·2044 N.
IV. 0·483 „ 0·1204 N.
V. 0·8966 „ 0·6833 AgBr.
VI. 0·5004 „ 0·2197 CO_2.†

	Theory.		Experiment.					
			I.	II.	III.	IV.	V.	VI.
Si....	28	2·77	2·53	—	—	—	—	—
Br_4 ..	320	31·76	—	—	—	—	32·40	—
C_{10} ...	120	11·91	—	—	—	—	—	11·88
N_{18} ...	252	25·00	—	—	25·23	24·92	—	—
S_8....	256	25·39	25·25	25·65	—	—	—	—
H_{32} ..	32	3·17	—	—	—	—	—	—
	1008	100·00						

---

* Experiments are in progress in my laboratory on the action of bromides of carbon and tin on thiocarbamide.

† Calcium chloride tube spoiled.

The difficulty experienced in separating the bromide of silver in a perfectly pure state sufficiently accounts for the slight excess of bromine; but the data generally lead to the conclusion that the substance includes the octothiocarbamide compound already obtained, together with an excess of carbon and nitrogen, doubtless resulting from the decomposition of another portion of the amide by the long-continued action of excess of silicon bromide at the boiling point of benzene. It is of interest to note that the expression,

$$SiBr_4,8(SCN_2H_4) : C_2N_2$$

closely agrees with the numbers obtained.

It seems probable that the product is a mixture, but that point will be investigated later on, as my immediate purpose was served when it was found that continued heating under the conditions stated led to decomposition, and not to increase in the proportion of silicon tetrabromide combined with the amide.

As there was some reason to suppose that slight access of air during the operation facilitated the decomposition just referred to, another experiment was made in a pressure tube with 6·1 grams of thiocarbamide, and silicon bromide and benzene in proportion. Air was expelled, the tube sealed, and then heated for 36 hours at 100°. At the end of this prolonged heating, and when the contents of the tube were cold, the solid product seemed perfectly homogeneous and closely resembled that already obtained. It was removed, broken up, washed with benzene, and the ratio of sulphur to nitrogen and carbon determined.

The ratio of sulphur to nitrogen was—

$$S : N_{1·976}.$$

and sensibly equal volumes of carbon dioxide and nitrogen were obtained on combustion with chromate of lead, therefore no such decomposition of thiocarbamide took place in the formation of this product, as occurred in a shorter time and at a lower temperature when air had access to the mixture.

The evidence obtained is conclusive as to the fact that 8 mols. of thiocarbamide withdraw but 1 mol. of silicon tetrabromide from a large excess of the latter when presented in benzene solution under the conditions specified above; and further, that the product is the result of chemical union between the compounds concerned. Whether the product is a single compound or a mixture must of course be determined by other means.

Mechanical solvents having failed to break up the substance, the action of anhydrous alcohol on it was next examined. When a quantity of the freshly prepared compound was boiled with carefully dehydrated ethyl alcohol almost complete solution took place, and only a minute quantity of a siliceous body separated. On cooling the solution in a well-closed flask, beautiful stellate groups or tufts of fine silky crystals separated. These groups of crystals sometimes resembled sea anemones in appearance; they were easily purified by several recrystallisations from alcohol. Although this compound gave the galena reaction with alkaline lead tartrate solution, which I recently described (Trans., 1884, p. 162), it did not possess any of the other characters of thiocarbamide.

On analysis, this substance proved to be a monobromo-compound of pentathiocarbamide, and its production is evidence that silicon tetrabromide, when made to act as described on the thiocarbamide, determines condensation of the latter to an extent which greatly exceeds that which we already know bromine alone can induce.

When the alcoholic solution from which the above-mentioned pentathiocarbamide derivative separated was distilled, a further crop was obtained, the mother-liquor from which when shaken up with two volumes of anhydrous ether separated into two layers. The heavier liquid, on standing, deposited crystals of the compound of ethyl bromide with thiocarbamide, and some of the bromethyl dithiocarbamide. The lighter layer was found to contain some of the bromethyl compounds and ethylic silicates.

A full account of the compounds obtained by the alcoholic treatment will shortly be laid before the Society; but the outline already given serves to explain the unexpected results obtained by the action of silicon tetrabromide on thiocarbamide, as it is evident that the silicon compound determines the condensation of the amide and then unites with the product. Any further discussion of the constitution of the octothiocarbamide compound with silicon tetrabromide must obviously be reserved until the results of the examination of the products of its action with alcohol have been stated in detail.

I have to thank my friend and former pupil, Mr. R. E. Doran, F.C.S., for much assistance in this work.

University Laboratory,
Trinity College, Dublin.

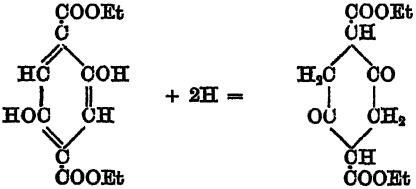
XXII.—*Notes on the recent papers by A. von Baeyer and Julius Thomsen: "On the Constitution of Benzene."*

By ALEX. K. MILLER, Ph.D.

To determine the constitution of benzene it is necessary according to Baeyer (*Ber.*, **19**, 1797) to establish—

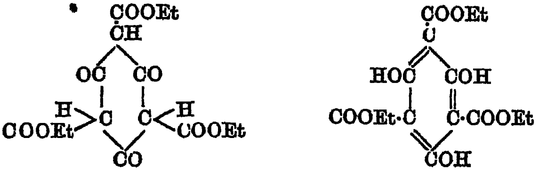
I. That hexahydrobenzene and hexamethylene are identical.
II. That ortho-, meta-, and para-substitution-derivatives of benzene furnish on reduction respectively 1 : 2, 1 : 3, and 1 : 4 substitution-derivatives of hexamethylene.
III. The symbols for benzene which II renders possible.
IV. The positions of the separable affinities.

I. Baeyer considers that the conversion of ethylic dihydroxytcrephthalate—a benzene-derivative—into ethylic succinosuccinate—a hexamethylene-derivative—by the action of nascent hydrogen, establishes the identity of hexahydrobenzene with hexamethylene. Using Kekulé's symbol, the reaction is expressed thus:—



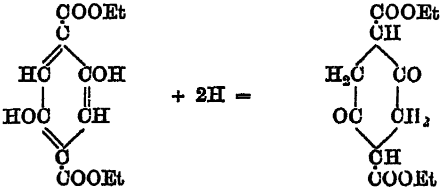
II. In support of the second point, namely, that ortho-, meta-, and para-substitution derivatives of benzene yield corresponding derivatives of hexamethylene on reduction, Baeyer cites the formation and behaviour (*a*) of ethylic succinosuccinate and (*b*) of ethylic phloroglucoltricarboxylate.

Baeyer's argument is that in the formation (*a*) of ethylic succinosuccinate, both the COOEt groups and the O atoms retain the para-position (for reaction see above); and that (*b*) in the case of phloroglucol-derivatives, the O atoms preserve the meta-position during the change of the so-called secondary into a tertiary ring, thus:—

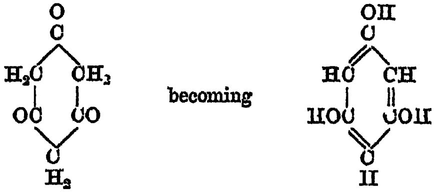


Secondary form. Tertiary form.

Now, on looking at the equation representing the first of these two changes, it will be noticed that in the conversion of the benzene-derivative into the *hexahydrobenzene*-derivative, not six but only two hydrogen-atoms are taken up. The reaction is therefore not a case of reduction or addition pure and simple, but is accompanied by an intramolecular change, according to Baeyer's own equation: yet Baeyer brings this forward as an argument in support of the proposition that ortho-, meta-, and para-substitution products of benzene yield, on *reduction*, 1 : 2, 1 : 3, and 1 : 4 derivatives of hexamethylene.

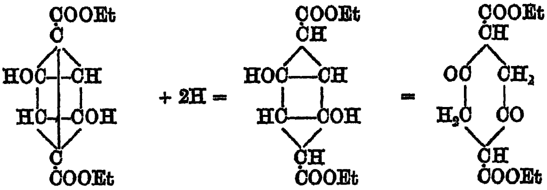


The second reaction upon which he bases his argument is not a case of reduction at all in the ordinary sense of the word, but involves an intramolecular change pure and simple :—



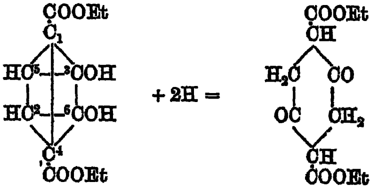
Reactions admittedly involving such intramolecular changes can scarcely be accepted as evidence either for or against any particular benzene formula, especially as we are altogether ignorant of the precise manner in which the isomeric change is brought about. If Baeyer's equation be accepted, the change may no doubt be regarded as involving merely a *migration* of hydrogen-atoms, but is not migration merely one of the many convenient terms in use for expressing changes we do not understand?

Baeyer does not attempt to discuss the two reactions in question with reference to any other symbol than Kekulé's; Ladenburg (*Ber.*, **19**, 973), however, has shown how the first may be represented by means of the prism formula; in his opinion, it is possible to express the reduction of ethylic dihydroxyterephthalate to ethylic succinosuccinate by the following symbols :—



Here, however, Ladenburg himself has fallen into a curious mistake in using his own symbol: if the six carbon-atoms of the prism be numbered so that each shall correspond with the carbon-atom bearing the same number in Kekulé's symbol, it will be evident that the above formula represents the *ortho*-dihydroxy-derivative of ethylic terephthalate, whereas it is the *para*-dihydroxy-compound which yields ethylic succinosuccinate.

If the attempt be made to represent the change from a paradihydroxy-derivative of ethylic terephthalate into ethylic succinosuccinate, employing the prism formula, an isomeric change must be assumed to occur.

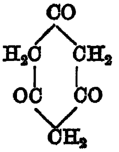


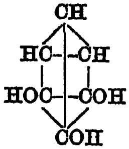
This change appears at first sight somewhat complicated, and therefore perhaps improbable; but on closer examination it will be found to be no more complicated than that involved in the reaction as represented by Baeyer, the most important difference being that Baeyer's equation indicates a migration of hydrogen-atoms, whilst according to the above an atom of oxygen migrates from position 6 to position 2. But it must be borne in mind that in the prism formula the carbon-atoms 6 and 2 are directly united, and that this migration of oxygen is simply from one carbon-atom to an adjacent carbon-atom; and, further, that since the molecule must be assumed to be changing form, that is, from a prism to a closed chain, this migration is necessary if the figure (originally symmetrical) is to retain its symmetry.*

---

* In connection with the question of symmetry, it may be pointed out that nearly all synthetical reactions involving the formation of benzene-derivatives from non-aromatic substances yield symmetrical products; the following examples may be mentioned in illustration of this: synthesis of mesitylene from acetone or from allylene; uvitic acid from pyruvic acid; 1 : 3 : 5 tribromobenzene by the action of

The change which Baeyer assumes to take place in the case of phloroglucol-derivatives in passing from the secondary to the tertiary form, may be represented in the same way:—





I do not offer this explanation in defence of the prism formula, but merely as one which might perhaps be brought forward as a last resource by the defenders of this symbol.*

III. In the third section of his paper, Baeyer brings forward his *one* argument against the prism formula. As the prism consists of two triangles united as in Fig. 1, it is evident that if in the formation of additive compounds two of the three *para*-lines of union—5 : 2, 1 : 4, 3 : 6—can be severed, a derivative of ditrimethylene will be obtained, which on further reduction cannot possibly yield a derivative of hexamethylene.

FIG. 1.

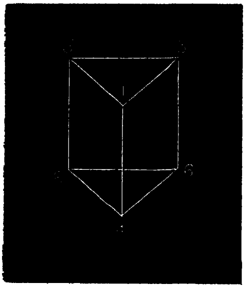
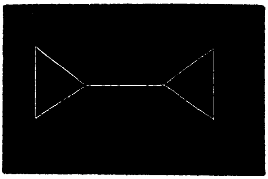


FIG. 2



If two elements present in the prism in the para-position to one another are also to occupy the positions 1 : 4 in the corresponding hexamethylene-derivative, the 1 : 4 union must vanish. If the same argument be applied to a second pair of para-atoms, a second para-union must go, and the product will no longer be capable of yielding a hexamethylene-derivative, Fig. 2. This is Baeyer's argument; and

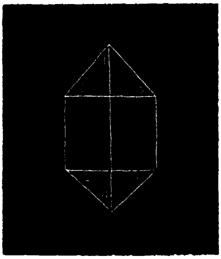
---

light on bromacetylene; trimesic acid from propargylic acid; quinol or hydroquinone by the distillation of succinates; and lastly the syntheses of ethylic succinosuccinate and of ethylic phloroglucoltricarboxylate. Reactions involving the employment of high temperatures or of very powerful reagents cannot of course be included.

* In the number of the *Berichte* (20, p. 62) which has come to hand since this paper was read, this argument has actually been brought forward by Ladenburg.

if he could cite a single case in which two atoms of hydrogen (or of any other monad radicle) could be introduced into a benzene compound, so that they take up the positions 1 : 4, and then repeat the process so that the second pair should take up the positions 2 : 5 or 3 : 6, he would be able to clearly disprove the prism formula. The only reaction, however, which he mentions in support of his argument, is the reduction of ethylic dihydroxyterephthalate to ethylic succinosuccinate, and this certainly does not fulfil the conditions mentioned. Only one pair of hydrogen-atoms is added, the rest of the reaction being a molecular change, which can scarcely be regarded as supporting either view, throwing no light whatever on the positions of the "latent bonds."

FIG. 3.



IV. Undoubtedly the most valuable section of the paper under discussion is the fourth, as it contains many new and interesting facts; but these for the most part cannot be regarded as throwing any light on the constitution of benzene. There is, however, one experiment to be noticed, which, according to Baeyer, proves the existence of at least *one* pair of double bonds in benzene. Commencing with terephthalic acid, he converts this by the action of nascent hydrogen into tetrahydroterephthalic acid, which readily takes up two atoms of bromine, yielding dibromohexahydroterephthalic acid. The problem is then to determine the positions of the two bromine-atoms; if it can be proved that these occupy the ortho-position to one another, it will also be proved that the two carbon-atoms to which the bromine-atoms are attached were doubly linked before the addition of the bromine, thus proving the presence of at least one pair of double bonds in benzene. This is Baeyer's argument, and it evidently takes for granted the non-existence of free affinities. In order to determine the position of the bromine-atoms, the compound was treated with silver oxide, and hydroxyl substituted for the bromine-atoms. On concentrating the solution, a syrup was left which would not crystallise, and his attempts to obtain a crystalline salt were equally unsuccessful. Having failed to get any results with the compound supposed to be dihydroxyhexahydroterephthalic acid, he tried the action of bromine on it; this gave a substance, the aqueous solution of which yielded a blue coloration with ferric chloride. He does not mention any other property of the substance, neither does he say whether he analysed it, but apparently he did not. He simply states that it was tetrabromocatechol, and concludes from this that there is at least one double union in benzene.

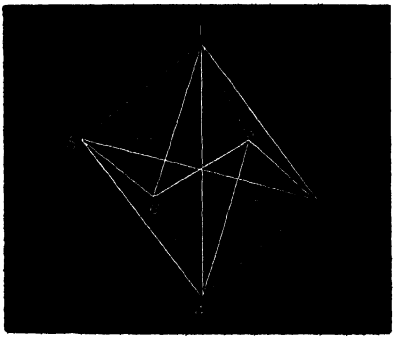
Even granting that the product in question is tetrabromocatechol, and granting also the non-existence of free affinities, the production of such a compound is only an argument in favour of, and no *proof* of, the existence of the double bond. Baeyer simply states that he *treated* the dihydroxy-acid with bromine, but does not say how he did this, or at what temperature; the reaction can scarcely be regarded as a normal one, and if this be admitted the reaction proves nothing.

It may also be pointed out that the same reactions are brought forward as proofs of propositions Nos. I, II, and III, and that they are only two in number, so that unless it is perfectly clear how the reactions take place, a single error in the explanation of either may upset three arguments out of four.

The last part of the research, that is, the examination of the additive compounds of benzene and its derivatives, can scarcely fail to yield results of considerable theoretical interest, but it is difficult to avoid the conclusion that the research leaves the question of the constitution of benzene just where it was before.

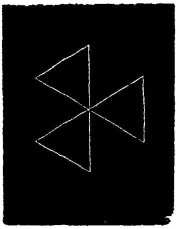
Julius Thomsen (*Ber.*, 19, 2944) has also recently contributed to the discussion on the constitution of benzene. In the symbol which he proposes, the six carbon-atoms represent the points of a regular octahedron. The arrangement of the bonds is best seen from the figure, in which the white lines indicate the way in which the carbon-

FIG. 4.

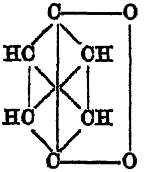


atoms are united, the dotted lines being added to complete the octahedron. The projection of this figure is a hexagon with diagonals, but Thomsen points out that his symbol differs from the ordinary diagonal formula, in that it is the projection of a solid figure, the essentials of which are the diagonal bonds, and these cannot be severed without the destruction of the molecule. The formation of additive compounds is explained by the severance of one, two, or three of the peripheral bonds, so that the nucleus of hexamethylene will be—

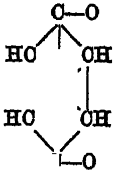
FIG. 5.



Thomsen's benzene symbol is, as he states, a symmetrical figure, which renders possible three and only three isomeric disubstitution-derivatives, namely, 1 : 2, 1 : 3, and 1 : 4, the positions 2 and 6, also 3 and 5, being identical in their relation to 1. These are the chief points which Thomsen brings forward in recommendation of his formula.* There are, however, some other points of interest in connection with this symbol, and which I think are of importance in connection with the subject of the constitution of benzene. Thomsen's formula differs from Kekulé's formula and from the prism formula, in that it renders possible four disubstitution-derivatives of hexamethylene, whilst three only are possible according to the other two symbols, assuming in each case that the substituents are attached to different carbon-atoms. Another difference is that quinone cannot be represented as a diketone, the formulæ—



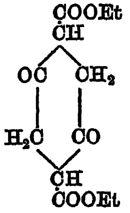
and



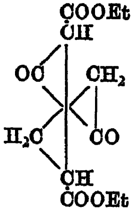
being alone possible. The greatest difficulty, however, is perhaps the representation of certain synthetical reactions, as for example, the synthesis of ethylic succinosuccinate, which is so readily shown by the symbols at present in use.

---

* It may be mentioned that the representation of the diagonal symbol as a regular octahedron is not new, and will be found in Laubenheimer's text-book (1884), where the above symbol for the hexamethylene nucleus is also given.



Symbol generally employed.



Thomsen's symbol.

Indeed the difficulties presented by this formula outweigh the advantages claimed for it by its author, and on this account it may be doubted whether it will commend itself to chemists.

City and Guilds of London Institute,
Central Institution.

XXIII.—*Agricultural Experiments with Iron Sulphate as a Manure during* 1886.

By A. B. Griffiths, Ph.D., F.R.S.E., Principal and Lecturer on Chemistry, School of Science, Lincoln, late Lecturer on Chemistry, Technical School, Manchester, &c.

This paper records a continuation of my experiments on the use of ferrous sulphate as a manure.

(1.) *Meadow Hay Crop.*

On referring to my last year's experiments (Trans., 1886, 117), it will be observed that grass land was improved by the use of iron sulphate. This year I have experimented with iron sulphate to see the quality and quantity of *hay* produced by the use of this manure. Two plots of land (of similar chemical and mechanical composition) were chosen of the same size and exposed to the same atmospheric influences (sunshine and rainfall). Both were manured first of all with farmyard manure (the same quantity on each plot). Upon each plot of land 16 lbs. of ordinary grass seed were used per acre. After the grass had made its appearance above ground, ½ cwt. of iron sulphate was used on one plot as a top-dressing, but the other plot did not receive any iron sulphate or other artificial manure. Very soon it was noticed that the grass manured with iron sulphate was growing far more rapidly than the grass not treated with the iron manure, and was of a beautiful green colour. At the end of the season, the harvest yielded the following results:—

Meadow Hay.

	Grown *with* iron sulphate.	Grown *without* iron sulphate.
Yield of meadow hay (*dry*).......	6962 lbs.	3496 lbs.

There is a difference, therefore, due to the addition of iron sulphate. The one manured with iron sulphate yielded 3 tons 2 cwts. of hay, and the land *not* treated with the iron manure only $1\frac{1}{2}$ tons of hay.

Fair samples of hay from each plot of land were submitted to analysis, when the following results were obtained:—

Meadow Hay (dried at 100°).

	Grown *with* iron sulphate.	Grown *without* iron sulphate.
Albuminoïds	13·01	9·68
Soluble carbohydrates............	48·29	46·21
Woody fibre	27·49	33·67
Fat	3·30	3·10
Ash	7 90	7·31
	99·99	100·00

From the above, it will be seen that there is a considerable increase in the percentage of albuminoïds and soluble carbohydrates in the hay grown with the iron manure. The table following gives the results of the analyses of the ash of each crop of hay:—

Ash of Meadow Hay.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Iron oxide, Fe_2O_3	4·46	1·22
Potash, K_2O	18·21	21·92
Soda, Na_2O	1·92	2·00
Lime, CaO	18·24	18·31
Magnesia, MgO	7·62	7·64
Silica, SiO_2	36·43	37·89
Phosphoric oxide, P_2O_5	7·67	5·36
Sulphuric oxide, SO_3	3·54	2·89
Chlorine	1·90	2·75
	99·99	99·98

It will be noticed from the above that in the ash of meadow hay grown with ferrous sulphate the percentage of iron oxide is greatly increased and so is the phosphoric oxide. It will be remembered that in my experiment last year it was found that the iron sulphate destroyed moss that infects grass land (Trans., 1886, 117).

(2.) *Mangel-wurzel Crops.*

The variety known as "Orange Globe" was used in the following experiments. Two plots of well-drained land were used, each of equal size, and exposed to the same atmospheric influences. Each plot was manured in the winter with 10 tons of farmyard manure. In the spring (April), the following mixture was applied broadcast on each plot of land (each plot receiving the following quantities

1 cwt. kainit,
1 „ nitrate soda,
4 cwts. superphosphate lime,
2 „ common salt,

per acre). On each plot of land, 5 lbs. of seeds were employed. When the young plants were ready they were "singled," the distance between plant and plant being about 12 inches. A month after "singling" a top-dressing of 1 cwt. of nitrate of soda and ½ cwt. of ferrous sulphate was applied to one plot A, whilst 1 cwt. of nitrate of soda only was used on plot B. At the end of the harvest (October), the following results were obtained:—

Mangel-wurzels.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Weight when gathered (root + leaf)........................	97,682 lbs.	78,369 lbs.

The two crops grew under like conditions as far as composition of soil, manures used, and atmospheric influences; except that one received a top-dressing of ½ cwt. of iron sulphate per acre, and the other crop had no dressing of the iron manure. The crop grown with the iron sulphate yielded 32 tons of roots, and the crop grown without iron sulphate yielded 26 tons of roots; there was, therefore, 6 tons in favour of the use of iron sulphate as a manure for mangel-wurzel crops. The next table gives the composition of the two crops:—

Mangel-wurzels.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Albuminoïds	2·89	1·90
Soluble carbohydrates............	11·21	9·32
Woody fibre.....................	1·98	2·05
Fat	0·25	0·21
Ash	1·52	1·00
Water	82·15	85·51
	100 00	99·99

From the above, it appears that the albuminoïds and soluble carbohydrates are increased in the crop grown with iron sulphate. The next table gives the analyses of the ashes of mangels from each plot:—

Ash of Mangel-wurzel Roots.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Iron oxide, Fe_2O_3	4·25	2·12
Potash, K_2O	43 98	16·69
Soda, Na_2O	8·24	8·43
Lime, CaO	12·99	13·62
Magnesia, MgO	4·00	4·90
Silica, SiO_2......................	8·24	8·91
Phosphoric oxide, P_2O_5	12 21	9·96
Sulphuric oxide, SO_3	2·92	1·02
Chlorine	3·14	4·05
	100·00	100·00

Ash of the Leaves (Mangels) gave, as far as the ferric oxide is concerned, the following results :—

	Grown *with* $FeSO_4$	Grown *without* $FeSO_4$.
Fe_2O_3	5·42 per cent.	3·29 per cent.

(3.) *Bean Crops* (Vicia faba).

This year I have for the third time tried the value of iron sulphate on bean crops. Two plots of land of equal size were chosen. Both plots received the same weight of farmyard manure, and upon each plot of land was sown the same number of bean seeds. After the plants were about 6 inches above ground, one plot was treated with ½ cwt. of commercial iron sulphate to the acre, and the other received no top-dressing.

The results obtained at the harvest were as follows :—

Bean Crop.

	Grown *with* $FeSO_4$.		Grown *without* $FeSO_4$.	
	Weight when gathered.	Weight when dry.	Weight when gathered.	Weight when dry.
Total weight of crop (grain + straw)	7016 lbs.	5920 lbs.	5192 lbs.	4726 lbs.

The crops of beans grown *with* a top-dressing of ferrous sulphate yielded 50 bushels, whilst the crop grown without iron sulphate gave only 30 bushels. The next two tables give the composition of each crop of beans (seeds and straw) :—

Bean Seeds.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Albuminoids	28·82	26·22
Soluble carbohydrates	47·00	44 63
Woody fibre	8·10	10·21
Fat	1·34	2·03
Ash	4·25	3·80
Water	10·48	13·11
	99·99	100·00

Bean Straw.

	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.
Albuminoïds	7·42	6·40
Soluble carbohydrates	38·25	36·25
Woody fibre	35·41	36·01
Fat	2·14	1·62
Ash	4·10	3·90
Water	12 67	15·80
	99·99	99·98

From the above tables, it is evident that the albuminoïds, soluble carbohydrates, and ash are increased in the crop grown with a top-dressing of iron sulphate. The next table shows the produce of three years' crops of beans.

Bean Crops.

	1883 crops.			1884 crops.			1886 crops.		
	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.
Bushels of grain	56	35	21	44	28	16	50	30	20

The following table shows the difference in the percentage of ferric and phosphoric oxides in the ashes of each crop:—

In Ashes of Entire Plants.

	1883 crops.			1884 crops.			1886 crops.		
	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.	Grown *with* $FeSO_4$.	Grown *without* $FeSO_4$.	Difference.
Fe_2O_3.	4·221	1·063	3·158	4·910	1 002	3·908	4·824	1·099	3·725
P_2O_5 .	41·902	37·941	3·961	40·831	37 814	3·017	40·651	37·424	3·227

The conclusions to be drawn are, that the iron sulphate has increased the yield of the three years' crops of beans (the crops each year grew under like conditions). The three years' crops of beans all indicate an *increase* of ferric oxide in the ashes of those plants grown *with* ferrous sulphate. Throughout all my experiments the iron oxide is increased in the ash by the use of the iron manure. This increase of iron in the plant increases the quantity of chlorophyll in the leaves (Trans., 1885, 46—55, "Estimation of Chlorophyll in the leaves of my crops," by Dr. W. J. Russell, F.R.S.). By increasing the chlorophyll, it is possible that the carbohydrates, albuminoids, &c., are increased as in the results obtained in this year's crops. It is well-known that chlorophyll is the active agent in plant-life which gives rise in the first instance to starch, and from this the various carbohydrates take their origin.

I have always recommended ½ cwt. of ferrous sulphate to the acre. Sir J. B. Lawes, F.R.S., kindly wrote me that he found the 1½ cwt. of iron sulphate per acre "*was rather too much, although it did not kill the plants.*"

(4). *Horticultural Experiments.*

It will be remembered that in my last paper on this subject before the Chemical Society, I stated that I found that ferrous sulphate was "a good manure for rose-trees."

I have also tried the iron manure this year with great success on palms and india-rubber trees. I had palms and india-rubber trees growing in the window of a room, and no direct sunlight ever came into that room. These plants struggled on through the winter. I made the following comparative experiments: one palm and one india-rubber tree were treated with ferrous sulphate, and one of each plant was not treated with the iron manure. The india-rubber tree treated with ferrous sulphate produced very large leaves of a dark green colour (even under the above unfavourable condition for plant-life); and the palm also produced a large quantity of leaves. The two plants not treated with ferrous sulphate lost nearly all their leaves; and the leaves that persisted through the winter were of a much lighter green colour than those treated with the iron manure.

On submitting the ashes of those leaves to analysis, the following percentage of ferric oxide was obtained in each case:—

Ashes of Palm (Chamaerops humilis) *and India-rubber Plant* (Ficus elastica).

	Grown *with* iron sulphate.		Grown *without* iron sulphate.	
	Palm.	India-rubber plant	Palm.	India-rubber plant.
Fe_2O_3	4·68 per cent	5·12 per cent.	2 99 per cent	2 87 per cent.

(5). *Antiseptic Powers of Ferrous Sulphate.*

I have already found that iron sulphate is an antiseptic agent of great value, destroying completely certain parasitic micro-organisms which attack our crops (Trans., 1886, 119; and, more fully, the *Chem News*, **53**, 255).

(6). *Ferrous Sulphate versus Kainit.*

It will be observed in all my published papers on this subject that in the ashes of those plants grown with ferrous sulphate the potash (K_2O) is chiefly lessened, and not the other constituents.

This year I have tried experiments in connection with this point. Two plots of land of the same size (an acre), and exposed to the same atmospheric influences, were each manured with 15 tons of farmyard manure in the autumn. Upon each plot was sown 6 cwts. of *potato tubers*. When the plants were fairly above ground, one plot, A, received a top-dressing of ½ cwt. of ferrous sulphate to the acre, and plot B 2 cwts. of kainit (containing 16 per cent. potash). At the end of the harvest, the following results were obtained:—

Potato Crops.

	A.	B.
Tubers	20,160 lbs. per acre	13,440 lbs per acre.
Haulm	6,831 „	4,362 „
Total weight of crop..........	26,991 „	17,802 „

From the above, the crop grown with a dressing of iron sulphate (½ cwt.) yielded 9 tons of tubers, and the other crop treated with 2 cwts. of kainit yielded only 6 tons of tubers. I do not attribute this great increase solely to the direct manurial value of ferrous sulphate. It will be remembered that in last year's paper it was proved that ferrous sulphate was a retentive agent for ammonia and phosphoric acid (Trans., 1886, 121); hence it may be that some of the properties of the farmyard manure were retained to a greater extent in the land treated with iron sulphate than in the land manured with kainit.

On submitting these crops to analysis, the following results were obtained:—

Potato Crops.

	A.	B.
Albuminoïds	3·92	2·24
Soluble carbohydrates	24·00	21·36
Woody fibre	1·61	1·00
Fat	0·29	0·21
Ash	1·50	1·21
Water	68·68	73·97
	100·00	99 99

It will be noticed that the albuminoids and soluble carbohydrates (soluble in dilute acids) are increased in the crop grown with ferrous sulphate as compared with the crop grown with the potash manure.

The next table shows the percentage of ferric and phosphoric oxides in the ashes of the two crops, and also the potash.

From Ashes of Potato Tubers.

	A.	B.
Iron oxide, Fe_2O_3	7·24 per cent.	5·22 per cent.
Phosphoric oxide, P_2O_5	18·31 „	16·54 „
Potash, K_2O	51·00 „	53·55 „

From Ash of Potato Haulm.

	A.	B.
Iron oxide, Fe_2O_3	4·52 per cent.	1·59 per cent.
Phosphoric oxide, P_2O_5	10·19 „	8·46 „
Potash, K_2O	26 63 „	28·96 „

From these results, it appears that the iron *does replace* the potash in this crop (potato), and also, judging from this investigation, the iron sulphate is a better manure than the kainit.

The crop treated with iron sulphate entirely resisted the attack of *Peronospora infestans*, whereas there were signs of disease in the crop manured with kainit. It may be that potash manures "help to foster the development and growth of parasitic fungi" (see the author's paper, *Chem. News*, **53**, 256). Professor Jamieson (*Chem. News*, **52**, 287) has shown that in certain cases potassium chloride acts as a "*plant poison.*" Jamieson's experiments have been confirmed to a certain extent by Dr. Munro (*Chem. News*, **53**, 2).

(7.) *The Size of the Experimental Plots.*

The area of each plot of land in all the above experiments was an *acre.* Therefore the yield in each case is so many lbs. per acre.

In conclusion, I wish to tender my best thanks to Sir Richard Owen, K.C.B., F.R.S., Sir J. B. Lawes, F.R S., Professor J. P. Cooke, LL.D. (Harvard University, U.S.A), and many other scientific friends for their kind letters and suggestions relating to this piece of research.

XXIV.—*The Action of Triphenylmethyl Bromide on Ethylic Sodiomalonate.*

By G. G. HENDERSON, M.A., B.Sc., Assistant to the Professor of Chemistry, University of Glasgow.

AT the suggestion of Professor Wislicenus, I began some months ago the investigation described in this paper, with the object of ascertaining if triphenylmethyl bromide acts on ethylic sodiomalonate, and of comparing the products of any action which might take place with those described by Allen and Kollicker (*Annalen*, **227**, 107) as resulting from the action of the former substance on ethylic sodioacetoacetate.

Both triphenylmethyl bromide and ethylic sodiomalonate can be prepared with ease. The former is obtained by adding bromine drop by drop to triphenylmethane at a temperature of 130—150°, pouring out the fused mass into a flat porcelain dish, dissolving it when cold in carbon bisulphide, and allowing it to crystallise out slowly in a current of dry air (Allen and Kollicker, *loc. cit*). The yield of pure triphenylmethyl bromide is very satisfactory. Ethylic sodiomalonate I prepared by adding the requisite quantity of sodium in fine wire to a solution of ethylic malonate in absolute ether. The reaction goes on slowly of itself, and is completed by the application of heat for a short time.

Preparation of Ethylic Triphenylmethylmalonate.

Ethylic sodiomalonate, obtained as above, suspended in absolute ether, was added in small portions at a time to a solution of triphenylmethyl bromide in absolute ether, contained in a flask attached to a reflux condenser, molecular proportions of the substances being used. The reaction which ensued began spontaneously, and was aided by gentle heating, being allowed to complete itself before each fresh addition of ethyl sodiomalonate. Finally the solution, which gradually assumed a reddish-yellow colour, was boiled for about an hour until its reaction was neutral to test-paper, and then filtered off from the precipitated sodium bromide, which was afterwards washed with ether. The washings were added to the original solution, and the ether was then distilled off. The thick, syrupy, orange-coloured liquid which remained was mixed with about an equal volume of absolute alcohol, when, after a short time, colourless crystals separated. These were redissolved in boiling absolute alcohol, and crystallised out on cooling in small shining colourless prisms; these melt at 133° and are sparingly soluble in cold alcohol, but more readily in ether and in boiling alcohol. Analysis of the crystals dried at 110° gave the following results:—

I. 0·25075 gram substance gave 0·7130 gram of CO_2 and 0·1490 gram of H_2O.

II. 0·2765 gram substance gave 0·7840 gram of CO_2 and 0·1620 gram of H_2O.

From these numbers, the following percentages are obtained:—

	I.	II.	Calculated for $C_{26}H_{26}O_4$.
C	77·56	77·39	77·61
H	6·58	6·51	6·47
O	—		15·92
			100·00

The composition of the crystals, therefore, corresponds with that calculated for *ethylic triphenylmethylmalonate*,

$$(COOC_2H_5)_2CH{\cdot}C(C_6H_5)_3,$$

and the formation of this substance may be represented by the following equation:—

$$(COOC_2H_5)_2CHNa + (C_6H_5)_3CBr = NaBr + (COOC_2H_5)_2CH{\cdot}C(C_6H_5)_3.$$

This reaction is not exactly similar to that which occurs when ethylic sodioacetoacetate is used, for in the latter case, whilst a substituted acetic acid is obtained, one half of the ethylic sodioacetoacetate is at the same time retransformed into ethylic acetoacetate (Allen and Kölliker, *loc. cit.*). On the other hand, I found that there was practically no ethylic malonate formed.

Preparation of β-Triphenylpropionic Acid.

To effect the hydrolysis of the ethereal salt just described, one part of the salt was heated on the water-bath for some time with about four parts of alcoholic potash; the solution was then evaporated to dryness, and the crystalline residue dissolved in a small quantity of water.

On adding hydrochloric acid, a white flocculent precipitate was formed, which was filtered off, washed, dried in bibulous paper, and then dissolved in boiling alcohol. On cooling, small colourless prismatic crystals separated; these melt at 177° and dissolve readily in alcohol and very readily in ether. Analysis of the crystals dried at 110° gave the following results:—

I. 0·1780 gram substance gave 0·5455 gram of CO_2 and 0·0985 gram of H_2O.

II. 0·1570 gram substance gave 0·4790 gram of CO_2 and 0·0805 gram of H_2O.

From these results, the following percentages are obtained:—

	I.	II.	Calculated for $C_{21}H_{18}O_2$.
C	83·42	83·21	83·44
H	6·14	6·12	5·96
O	—	—	10·60
			100·00

It appears therefore that during hydrolysis the ethylic triphenylmethylmalonate is partly decomposed, 1 mol. of CO_2 being eliminated, and that, instead of a substituted malonic acid, *β-triphenylpropionic acid*, $C(C_6H_5)_3{\cdot}CH_2{\cdot}COOH$, is obtained.

The reaction may be represented thus:—

$$(COOC_2H_5)_2CH{\cdot}C(C_6H_5)_3 + 3KOH = COOK{\cdot}CH_2{\cdot}C(C_6H_5)_3 + K_2CO_3 + 2C_2H_5{\cdot}OH.$$

It may be noted that the presence of potassium carbonate as one of the products of the reaction was proved.

Attempts to obtain a substituted malonic acid by hydrolysis of the ethereal salt with cold aqueous and with alcoholic potash have hitherto been unsuccessful.

Potassium triphenylpropionate, $C_{21}H_{17}O_2K + H_2O$, crystallises in colourless prisms, readily soluble in water and in alcohol.

Sodium triphenylpropionate, $C_{21}H_{17}O_2Na + H_2O$, crystallises in tufts of delicate colourless interlacing needles, which dissolve very easily in water and readily in alcohol. 0·2260 gram of the salt, dried over sulphuric acid, gave on analysis 0·0120 gram = 5·31 per cent. of H_2O, and 0·0465 gram of Na_2SO_4 = 6·66 per cent. of Na. For the formula given, the calculated numbers are 5·26 per cent. of H_2O and 6·72 per cent. of Na.

Barium triphenylpropionate, $(C_{21}H_{17}O_2)_2Ba + H_2O$, is obtained as a white crystalline precipitate which is only sparingly soluble in boiling water. In boiling alcohol, it dissolves pretty readily, and separates out on cooling in clusters of small white crystals. 0·1720 gram of the crystals, dried over sulphuric acid, gave on analysis 0·0040 gram = 2·4 per cent. of H_2O, and 0·0525 gram of $BaSO_4$ = 17·95 per cent. of Ba. Calculated for the formula given, H_2O = 2·37 per cent., Ba = 18·09 per cent.

Silver triphenylpropionate, $C_{21}H_{17}O_2Ag$, is obtained as a white microcrystalline precipitate, which gradually turns pink when exposed to the air. It is insoluble in water, but dissolves in a large quantity of boiling alcohol, from which it separates on cooling in small, feathery, whitish crystals; these also become dark pink by degrees. Analyses of the salt dried at 110° gave the following numbers:—

I. 0·1770 gram substance gave 0·3990 gram of CO_2, 0·0685 gram of H_2O, and 0·0465 gram of Ag.

II. 0·2495 gram substance gave 0·5610 gram of CO_2, 0·0987 gram of H_2O, and 0·0655 gram of Ag.

From these results, the following percentages are obtained:—

	I.	II.	Calculated for $C_{21}H_{17}O_2Ag$.
C	61·47	61·32	61·61
H	4·30	4·39	4·16
Ag........	26·27	26·25	26·41
O	—	—	7·82
			100·00

The lead and copper salts are obtained as white and blue precipitates respectively, and are insoluble in water.

Ethylic triphenylpropionate, $C_{21}H_{17}O_2{\cdot}C_2H_5$, is easily obtained by suspending the silver salt in alcohol, adding the necessary quantity of ethylic iodide, and boiling for some time. The solution is filtered hot from the precipitated silver iodide, and as it cools colourless prismatic crystals separate. These, when purified by recrystallisation from alcohol, in which they are readily soluble, melt at 81°; they dissolve also very readily in ether. Analyses of the crystals, dried *in vacuo* over sulphuric acid, gave the following results:—

I. 0·1965 gram substance gave 0·6010 gram of CO_2 and 0·1179 gram of H_2O.

II. 0·1850 gram substance gave 0·5665 gram of CO_2 and 0·1132 gram of H_2O.

From these figures, the following percentages are calculated:—

	I.	II.	Calculated for $C_{23}H_{22}O_2$
C	83·39	83·51	83·63
H	6·66	6·80	6·66
O	—	—	9·71
			100·00

At present I am engaged in further investigation of the derivatives of ethylic triphenylmethylmalonate, and hope to be able to communicate the results to the Society before long.

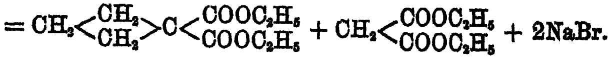
I take this opportunity of expressing my best thanks to Professor Wislicenus for the kind advice and assistance he gave me during the progress of this work.

XXV.—*The Synthetical Formation of Closed Carbon-chains.* Part II, continued. *Some Derivatives of Tetramethylene.*

By H. G. Colman, B.Sc., and W. H. Perkin, Jun., Ph.D.

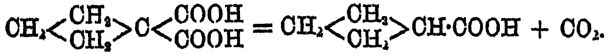
In a former communication to this Journal on the tetramethylene-derivatives (Perkin, this vol., p. 1), it was shown that substances of this nature are obtained when the sodium compound of ethyl malonate is heated with trimethylene bromide, thus:—

$$2CHNa(COOC_2H_5)_2 + CH_2Br{\cdot}CH_2{\cdot}CH_2Br$$



$$= CH_2{<}\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}C{<}\genfrac{}{}{0pt}{}{COOC_2H_5}{COOC_2H_5} + CH_2{<}\genfrac{}{}{0pt}{}{COOC_2H_5}{COOC_2H_5} + 2NaBr.$$

The ethyl tetramethylenedicarboxylate thus formed on hydrolysis yields the corresponding acid, which, when distilled, splits up into tetramethylenemonocarboxylic acid and 1 mol. CO_2 :—

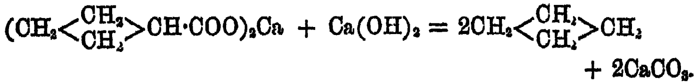


$$\text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{C}<\substack{\text{COOH}\\ \text{COOH}} = \text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH}\cdot\text{COOH} + \text{CO}_2.$$

The proof that this acid really has the constitution here assigned to it, was discussed in the above-mentioned paper.

In order to accomplish, however, the chief end of this research, namely, the formation of tetramethylene itself, it was now necessary to eliminate another mol. of CO_2.

The first method which suggested itself is the dry distillation of calcium tetramethylenemonocarboxylate with lime :—

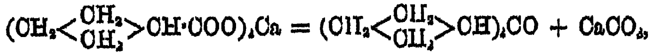


$$(\text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH}\cdot\text{COO})_2\text{Ca} + \text{Ca(OH)}_2 = 2\text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH}_2 + 2\text{CaCO}_3.$$

We have therefore carefully studied this reaction, and found, contrary to our expectations, that no tetramethylene is formed in this way. The examination of the products of this decomposition has led, however, to the isolation of some interesting derivatives of tetramethylene, a short account of which we wish to bring before the Society.

When calcium tetramethylenemonocarboxylate is distilled with lime, gas is evolved, and at the same time a light brown oil distils over. The gas proved on analysis to be a mixture of ethylene, hydrogen, marsh-gas, and carbonic oxide, and the oil was found to contain two new ketones, namely, ditetramethylene ketone and methyltetramethylene ketone.

The first of these two ketones is evidently formed by the decomposition of the calcium salt alone, according to the equation—



$$(\text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH}\cdot\text{COO})_2\text{Ca} = (\text{CH}_2<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH})_2\text{CO} + \text{CaCO}_3,$$

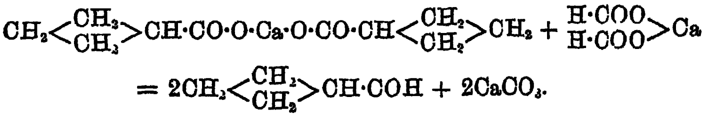
a reaction exactly similar to the formation of benzophenone by the dry distillation of calcium benzoate.

The second of these compounds, that is, methyltetramethylene ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}<\substack{\text{CH}_2\\ \text{CH}_2}>\text{CH}_2$, is evidently formed by a much more complicated reaction, in which one tetramethylene-group must in some way be reduced to methyl.

At first sight the formation of this compound seems somewhat singular, but several similar cases have been noticed in the fatty series. Thus calcium butyrate gives on distillation not only butyrone or dipropyl ketone, but also methylpropyl ketone (Friedel, *Annalen*, **108**, 125). Calcium isobutyrate, in like manner, gives a mixture of diisopropyl ketone and methylisopropyl ketone (Barbaglia and Gucci, *Ber.*, 13, 1572).

During these experiments, it was thought necessary, for reasons which will be stated later on, to prepare tetramethylene aldehyde.

This substance is obtained in the usual way by the distillation of a mixture of calcium tetramethylenemonocarboxylate with calcium formate—



$$\mathrm{CH_2{<}\substack{CH_2\\CH_2}{>}CH{\cdot}CO{\cdot}O{\cdot}Ca{\cdot}O{\cdot}CO{\cdot}CH{<}\substack{CH_2\\CH_2}{>}CH_2 + \substack{H{\cdot}COO\\H{\cdot}COO}{>}Ca}$$
$$\mathrm{= 2CH_2{<}\substack{CH_2\\CH_2}{>}CH{\cdot}COH + 2CaCO_3.}$$

The following is a detailed description of the experiments performed during this investigation.

The distillation of the calcium tetramethylenemonocarboxylate and lime was carried out as follows:—

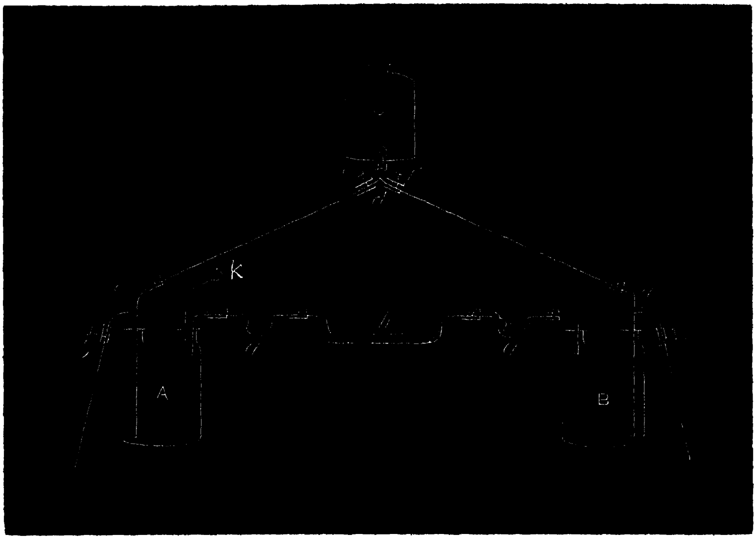
The calcium salt and the lime were well ground up together and filled into a broad piece of combustion tubing, which was closed at one end. This was then heated in an ordinary combustion furnace, beginning from the sealed end.

After a short time, and long before the tube had become red hot, a considerable amount of gas came off, which, after passing through a cooled flask, in order to collect the oil, was led into an apparatus described below. As a preliminary examination of a small quantity of the gas showed that it was a mixture, part of which was absorbed by bromine, a special apparatus was constructed, so as to subject the gas to the action of bromine until nothing further should be dissolved.

The accompanying figure shows the arrangement of this apparatus, and the following are the details of construction.

A and B are two Woulffe's bottles of 5 litres capacity, each having two necks. Through one neck of each passes a tube *a a'*, to which, just above the india-rubber stopper, a side tube is fused, the latter being bent down as shown, and connected by india-rubber tubing with a glass tube reaching down below the bottom of the Woulffe's bottle. At the india-rubber joints are screw pinchcocks, *b* and *c*. The tubes *a a'* are connected by bent glass tubes to the Y-tube *d*, and thus to the vessel C. The india-rubber joints at the ends of this Y-tube are closed by pinchcocks *e* and *f*. The vessel C is always kept full of water.

In the second mouth of each Woulffe's bottle is another tube, bent at right angles, connected with a bulb tube, *g*, and each of these bulb tubes is connected by the other end to the tube *h*, which is 30 cm. long, and nearly filled with broken glass and bromine (50 grams). In each of the bulb tubes is placed a small quantity of water, so that they serve to indicate the speed at which the gas is passing, and also to keep back to some extent the bromine vapour carried along with the gas.



In the second mouth of the bottle A is another tube, by means of which the gas to be examined is passed into the apparatus. When not in use this is closed by the india-rubber tube and pinchcock *k*.

All the india-rubber joints are carefully wired, and those which have at any time to be in contact with bromine vapour are previously soaked in paraffin.

Before using the apparatus, it is necessary to drive out the air. The vessels A and B, and tubes *a a'*, and all connections are filled with water, carbonic anhydride is then passed in through *k*, the pinchcock *b* being opened to allow water to siphon out as fast as gas comes in. When A is about half full of gas, *k* and *b* are closed, the pinchcock *e* is opened, and water thus passes into A, and forces the gas through the indicator *g*, over the bromine, into the Woulffe's bottle, B. The pinchcock *c* is also opened, so that as gas comes into B water siphons out. When as much gas as possible has been driven from A to B, *e* and *c* are closed, and *f* opened, and one of the india-rubber stoppers in B slightly loosened, by which means the gas is forced out into the air. When all is out the stopper is forced tightly in again, and this series of operations repeated four or five times, by which time all the air has been driven out and replaced by carbonic anhydride.

In order to pass the gas from the distillation tube into the apparatus, the tube leading from the condensing flask is connected with one end of a T-joint, a second end being connected to the Woulffe's bottle, A, by the tube *k*, and the third connected to a tube dipping under mercury, and closed by a pinchcock. When the tube is heated the latter pinchcock is opened, and the gas evolved collected over mercury until it is found to be free from air, when *k* is opened, and the other pinchcock closed. The gas then passes into A, and *b* is opened to allow water to siphon out. When the gas ceases to come off, *k* and *b* are closed, and *e* and *c* opened, and the gas forced from A to B. When A is empty, *e* and *c* are closed, and *f* and *b* opened. Water thus runs into B, and siphons out of A, so that the gas is forced back from B over the bromine again into A; *f* and *b* are then closed, and *e* and *c* opened, and this cycle of operations repeated as often as required.

The apparatus worked in a way which left nothing to be desired, never causing the slightest trouble after it had once been put together. The operation of reversing only takes a quarter of a minute, and, as will be seen, simply consists in closing two pinchcocks and opening two others. By using screw pinchcocks the flow of the gas can be regulated very exactly. To keep the vessel C full of water, it was connected with the water-tap by an india-rubber tube.

On passing the gas over the bromine for the first time, the volume was reduced to about one-third. A further very slight absorption took place the second time, but although it was passed over four times more, no further absorption took place.

During the operation, a small quantity of bromine vapour is carried along with the gas, though the water in the indicators serves to retain the greater part.

To disconnect the tube *h*, containing the bromine and absorbed gas, the india-rubber tube between the indicator nearest A and the tube *h* is closed by a pinchcock, the gas having previously been passed into A. The tube *h* can then be taken away, and the unabsorbed gas is thus prevented from escaping, and no air can get into it. When any of the gas is required for analysis, it can be taken out through the tube *k*.

Nature of the Absorbed Gas.

In order to determine as far as possible the nature of that part of the gas which was absorbed by the bromine, the contents of the tube, which still contained a considerable excess of bromine, were treated with sodium thiosulphate solution, until an almost colourless heavy oil remained. This was extracted with ether, the ethereal solution dried over calcium chloride, filtered, and the ether distilled off. Nearly

20 grams of a brownish oil were thus obtained, which the subsequent examination showed to be almost pure ethylene bromide.

At the first distillation, the whole went over between 125° and 135°, and on redistillation 10 grams of oil were easily obtained, boiling constantly at 131·5°.

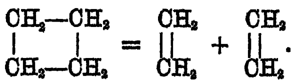
A bromine determination made by Carius' method gave the following numbers:—

Substance, 0·4576; AgBr, 0·9061; Ag, 0·0044.

	Calculated for $BrCH_2{\cdot}CH_2Br$.	Found.
Br	85·11	84·96

That the oil really was ethylene bromide was also shown by heating it with alcoholic potash, when a gas was evolved with the characteristic odour of acetylene, which gave a reddish-brown precipitate with ammoniacal cuprous chloride.

The formation of ethylene, unaccompanied by other unsaturated hydrocarbons, by the dry distillation of calcium tetramethylenemonocarboxylate with lime, is interesting, inasmuch as it is probably a product of decomposition of the tetramethylene first formed, thus:—



It is, however, remarkable that this decomposition should take place at so low a temperature.

Examination of the Gas unabsorbed by Bromine.

A preliminary examination was made in order to determine approximately the constituents of this gas, and for this purpose it was subjected to the action of various absorbing agents. After the absorption of carbonic anhydride by caustic potash, the gas was found to be acted on by ammoniacal cuprous chloride, showing the presence of carbonic oxide, and to be absorbed in a very marked manner by spongy palladium, indicating the presence of hydrogen.

Quantitative experiments were then made with the following results:—

I. 76·3 c.c. were reduced after absorption by potash to 74·9 c.c.

This 74·9 c.c., on treatment with ammoniacal cuprous chloride, lost further 1·1 c.c.

38·4 c.c. of residue when passed over spongy palladium were reduced to 7·2 c.c.

II. A second determination of the carbonic anhydride and carbonic oxide was made with the following results:—

72·6 c.c. were reduced after absorption by potash to 71·6 c.c.

This 71·6 c.c., on treatment with ammoniacal cuprous chloride, lost further 1·2 c.c.

The composition of the gas found from these analyses was as follows:—

	I.	II.
CO_2	1·83	1·38
CO	1·44	1·65
H	78 84	—
Unabsorbed......	18·14	—
	100·25	—

The unabsorbed part of the gas, as will be seen later on, was methane, together with a certain amount of air introduced from the tap-water.

From these experiments, it seems that no tetramethylene was formed.

It next appeared necessary to repeat these experiments with a sample of gas prepared at as low a temperature as possible; for this purpose, a mixture of 5 grams of calcium tetramethylenemonocarboxylate with 10 grams of slaked lime was very gently heated in a combustion furnace, and the gas evolved collected in tubes. A plug of lime in the front of the tube, which was not heated, served to absorb the oil formed.

	Volume.	Pressure.	Temp.	Vol. at 0° and 1 M. pressure.
Original gas employed	114·12	144·27	10·1	15·32
After addition of air and oxygen..	384·42	413 11	10·2	153·15
After explosion	354·13	377·80	10·2	130·52
After absorption of CO_2.........	349·95	371·30	10·8	128·60

II.

	Volume.	Pressure.	Temp.	Vol. at 0° and 1 M. pressure.
Original gas employed	118·53	139·42	13·3	15·76
After addition of air and oxygen..	385·37	403·94	13·8	148·53
After explosion....	354·64	372·06	14 8	125·31
After absorption of CO_2.........	348·52	369·56	13·1	122·91

Into these tubes, a coke bullet, saturated with bromine, was then passed, in order to absorb the ethylene, and it was found that the volume was reduced to one-third. After the removal of the excess of bromine by a potash bullet, the gas was analysed by Bunsen's method with the result given in the preceding tables.

Analysis I was made from a sample taken at the beginning, and Analysis II from a sample taken at the end of the operation.

In calculating the results, it was thought that the very laborious after-explosions with hydrogen might be avoided by directly determining the amount of carbonic oxide by absorption, and then subtracting this from the volume of gas employed, making corresponding corrections in the above numbers.

The amount of CO in several samples was found to vary from 1·5 to 1·6 per cent.

The gas used in Analysis I was found to contain 3·6 per cent. of air, the amount being determined by absorption of the oxygen by pyrogallol.

Allowing for these corrections, the following is the result of the two analyses:—

	I.	II.
Air	3·60	—
Hydrogen	84·08	84·4
Methane	10·84	13·3
Carbonic oxide ..	1·60	1·6
	100·12	99·3

It appears therefore that, even with these precautions, *no* tetramethylene is formed.

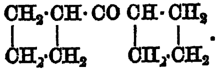
Examination of the Oil.

The oil formed by the dry distillation was now carefully examined. In order to free it from water, it was first dissolved in a little ether, the excess of water separated by a separating funnel, and the ethereal solution dried over calcium chloride. After filtering and distilling off the ether, about 20 grams of a dark brownish oil remained; this was submitted to fractional distillation, when nearly the whole went over between 100° and 250° as a colourless oil, which possessed in a marked manner the pungent odour of peppermint. On refractionating, a small quantity of a limpid oil, smelling somewhat like petroleum, came over below 120°; the quantity was unfortunately too small for examination. On further distillation, it was noticed that the thermometer remained for a short time fairly constant at about 135°, and then again at about 200°, and for this reason two chief fractions, 120—150° and 180—210° were collected.

The fraction boiling from 180° to 210°, which weighed about 8 grams, was first examined. After twice refractionating, by far the greater part passed over between 200 and 210°, and on repeated distillation an oil was at last obtained which boiled constantly at 204—205°. On analysis, this gave the following numbers:—

I. Substance, 0·1497 gram; CO_2, 0·4283 gram; H_2O, 0·1394 gram.

II. Substance, 0·1045 gram; CO_2, 0·2990 gram; H_2O, 0·0980 gram.

	Calculated for 	Found.	
		I.	II.
C..........	78·26	78·03	78·03
H..........	10·14	10·34	10·42

It thus appears that this compound is ditetramethylene ketone, which would be the normal product of the dry distillation of calcium tetramethylenemonocarboxylate alone.

$$(CH_2{<}^{CH_2}_{CH_2}{>}CH{\cdot}COO)_2Ca = (CH_2{<}^{CH_2}_{CH_2}{>}CH)_2CO + CaCO_3.$$

This ketone is a colourless oil, with a pungent peppermint-like odour, boiling at 204—205°. It combines easily with sodium hydrogen sulphite, forming a white, beautifully crystalline compound, which is fairly soluble in water, and instantly decomposed by acids. The formation of this compound is rather remarkable, as usually only methyl ketones combine with sodium hydrogen sulphite.

With acetate of phenylhydrazine, the dilute alcoholic solution of the ketone gives a yellow oily precipitate, which is probably the hydrazine compound, but as it did not crystallise it was not further examined. It has often been noticed in such cases that when the hydrazine compound is an oil, the hydroxylamine-derivative can be used with advantage. In order to test this, a solution of 1 gram of the ketone (b. p. 202—208°) in dilute alcohol was allowed to stand with an excess of hydroxylamine solution for eight days. Water and a few drops of dilute hydrochloric acid were then added, and the oil which separated extracted two or three times with ether.

After washing with water, drying over calcium chloride, and distilling off the ether, a colourless syrup was obtained, which did not crystallise until it had stood for four weeks over sulphuric acid in a vacuum. It was purified by spreading it out on a porous plate, and was then obtained as a white crystalline solid, melting at 51°. The following results were obtained on analysis:—

Substance, 0 2066; CO_2, 0·5341; H_2O, 0 1881.

For nitrogen: substance, 0·3200; N = 24·5 c.c.; temp. = 8·5°; bar., 758 mm.*

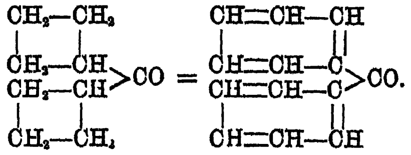
	Calculated for $C_9H_{15}NO$.	Found.
C	70·59	70·50
H	9·80	10·11
N	9·15	9·19

Ditetramethylene ketone is isomeric with the following compounds:—

Phorone, b. p. 196°.
Isophorone, b. p. 208—212°.
Camphorphorone, b. p. 202—205°.
Diallylacetone, b. p. 175°.

Bromine reacts easily with ditetramethylene ketone, but always with evolution of hydrogen bromide, a proof that it really contains two tetramethylene-rings, and is not an unsaturated compound.

Ditetramethylene ketone is interesting as being that derivative of tetramethylene which corresponds with benzophenone in the benzene series.



Ditetramethylene ketone. Benzophenone.

The fraction of the original oil boiling at 120—150° was next examined.

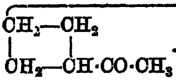
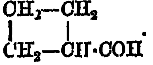
This fraction being much smaller than that of the fraction 180—210°, considerable difficulty was experienced in obtaining from it a substance having a constant boiling point. After repeated refractioning, however, an oil was finally isolated boiling at 136—137°, possessing in an even more marked degree than the ditetramethylene ketone the odour of peppermint. On analysing it the following numbers were obtained:—

I. Substance, 0·1084 gram; CO_2, 0·2888 gram; H_2O, 0·0981 gram.

II. Substance, 0·1374 gram; CO_2, 0·3661 gram; H_2O, 0·1262 gram.

---

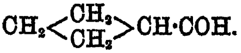
* The nitrogen determination was made with a portion which had remained for four days over sulphuric acid in a vacuum, but which had not then crystallised.

	Calculated for		Found.	
			I.	II.
C	73·47	71·43	72·66	72·66
H	10·20	9·52	10·20	10·05

Although these numbers are not so good as could be desired, there can be no doubt that this substance is methyl tetramethylene ketone, or acetyltetramethylene.

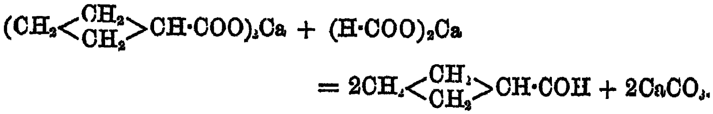
The only substance which has an analogous constitution is tetramethylene aldehyde, and in order to prove that these were really different tetramethylene aldehyde was prepared and examined, as will be shown in the next section.

Tetramethylene ketone combines very easily with sodium hydrogen sulphite, forming a beautifully crystalline substance, easily soluble in water. When treated with phenylhydrazine, a yellow compound is produced, which is probably the hydrazine compound. An oxime is also easily produced when the alcoholic solution of the ketone is treated with hydroxylamine, but as this could not be obtained in a crystalline condition it was not further examined.

Tetramethylene Aldehyde,  $\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH{\cdot}COH}$.

In order to prepare this compound, equal parts of calcium tetramethylenemonocarboxylate and calcium formate were finely powdered, intimately mixed, and filled into a combustion-tube drawn out at one end. The tube was then carefully heated, when a light oil distilled over, which was collected in a flask inserted in a freezing mixture.

The following equation represents the formation of the aldehyde:—



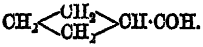
$$(\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH{\cdot}COO})_2\mathrm{Ca} + (\mathrm{H{\cdot}COO})_2\mathrm{Ca} \\ = 2\mathrm{CH_2}{<}\substack{\mathrm{CH_2}\\ \mathrm{CH_2}}{>}\mathrm{CH{\cdot}COH} + 2\mathrm{CaCO_3}.$$

During the distillation, a quantity of gas was evolved, and, particularly towards the end of the operation, a heavy brownish oil distilled over, accompanied by thick white fumes.

In fractioning the product, it was easily separated into two portions, one boiling between 100° and 130° and the other between 130° and 230°. The fraction boiling between 100° and 130° was then well shaken with sodium hydrogen sulphite, when in a short time almost the whole solidified to a mass of crystals. These were pressed, dried on a porous plate, and washed with a little alcohol, when a beautiful, silky crystalline mass was left. This compound was next dissolved in a little water, and mixed with an excess of sodium hydrogen carbonate solution, which caused decomposition and precipitation of the aldehyde. The latter was extracted with ether, and the ethoreal solution rapidly dried over calcium chloride; the ether distilled off, and the residual oil fractioned.

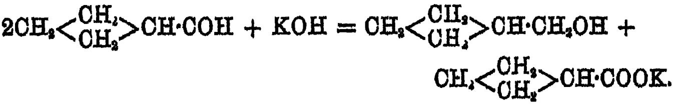
In this way a colourless oil was obtained possessing the characteristic pungent odour of the aldehydes; on twice refractioning, it boiled at 115—117°. The following is the result of an analysis:—

Substance, 0·1417; CO_2, 0·3696; H_2O, 0·1256,

	Calculated for  $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot COH.$	Found.
C.............	71·43	71·13
H.............	9·53	9·86

The odour of tetramethylene aldehyde closely resembles that of isobutylaldehyde. It possesses all the usual properties of an aldehyde. When shaken with a solution of rosaniline hydrochloride which has been decolorised by sulphur dioxide, a purple coloration is produced. It reduces ammoniacal silver nitrate with great ease, and combines readily with phenylhydrazine and hydroxylamine. When heated with alcoholic potash, it seems to behave more like an aromatic than a fatty aldehyde. A small quantity of the substance, when heated in this way, was transformed into a neutral compound and an oily acid; the latter possessed unmistakably the odour of tetramethylenemonocarboxylic acid.

The reaction is therefore probably the following:—



$$2CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot COH + KOH = CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CH_2OH + CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot COOK.$$

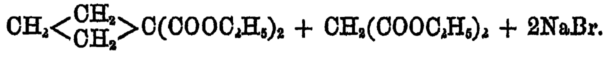
Owing to the small amount of material at our disposal, it was, unfortunately, not possible to oxidise this aldehyde, and thus obtain tetramethylenemonocarboxylic acid in quantity sufficient to prove its identity; but from the above there would appear to be no grounds for doubting that this substance is really tetramethylene aldehyde.

XXVI.—*The Synthetical Formation of Closed Carbon-chains.* Part III. *Some Derivatives of Pentamethylene.*

By W. H. Perkin, Jun., Ph.D.

In Part II of this research (this vol., p. 1), I showed that when the sodium compound of ethylic malonate is treated with trimethylene bromide, ethylic tetramethylenedicarboxylate (1, 1) is formed thus:—

$$2CHNa(COOC_2H_5)_2 + BrCH_2{\cdot}CH_2{\cdot}CH_2Br =$$



$$CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 + 2NaBr.$$

I also mentioned that this substance was not the only product of the reaction, a high boiling oil being also formed which always remained behind in the retort on distilling off the ethylic tetramethylenedicarboxylate.

The further examination of this oil has shown that it is ethylic pentane-$\omega_2\omega_2$-tetracarboxylate, the product of the direct action of 1 mol. of trimethylene bromide on 2 mols. of the sodium compound of ethylic malonate; thus:—

$$2CHNa(COOC_2H_5)_2 + BrCH_2{\cdot}CH_2{\cdot}CH_2Br =$$
$$(COOC_2H_5)_2CH{\cdot}(CH_2)_3{\cdot}CH(COOC_2H_5)_2 + 2NaBr.$$

Ethylic pentane-$\omega_2\omega_2$-tetracarboxylate.

This substance on hydrolysis is easily converted into the free pentanetetracarboxylic acid, and on heating the latter at 200°, it is resolved into normal pimelic acid and 2 mols. CO_2; thus:—

$$(COOH)_2CH{\cdot}(CH_2)_3{\cdot}CH(COOH)_2 = COOH{\cdot}(CH_2)_5{\cdot}COOH + 2CO_2.$$

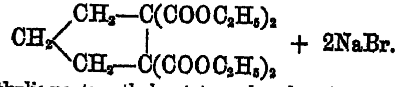
Pentane-$\omega_2\omega_2$-tetracarboxylic acid. Pimelic acid

The formation of normal pimelic acid by this simple decomposition shows at once that ethylic pentane-$\omega_2\omega_2$-tetracarboxylate must have the constitution assigned to it above.

If this substance be now mixed with a solution of sodic ethylate in ether, a disodium compound is formed, which, when treated with bromine, is directly converted into ethylic pentamethylenetetracarboxylate (1, 1, 2, 2). This simple change takes place according to the following equation:—

$$(COOC_2H_5)_2CNa{\cdot}(CH_2)_3{\cdot}CNa(COOC_2H_5)_2 + Br_2 =$$

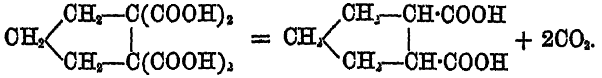
Ethylic pentane-$\omega_2\omega_2$-tetracarboxylate.



$$CH_2{<}\begin{matrix}CH_2{-}C(COOC_2H_5)_2\\ |\\ CH_2{-}C(COOC_2H_5)_2\end{matrix} + 2NaBr.$$

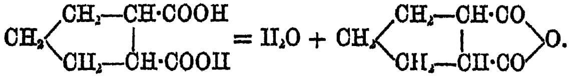
Ethylic pentamethylenetetracarboxylate (1, 1, 2, 2).

On hydrolysis, this substance yields the free pentamethylene tetracarboxylic acid (1, 1, 2, 2), which in its turn is easily converted (when heated at 200°) into pentamethylenedicarboxylic acid (1, 2) and 2 mols. CO_2; thus:—



Pentamethylenetetracarboxylic acid (1, 1, 2, 2). Pentamethylenedicarboxylic acid (1, 2).

This acid is the orthodicarboxylic acid of pentamethylene, corresponding with phthalic acid of the benzene series, and is therefore easily split up on heating into its anhydride and water, thus:—



Anhydride of pentamethylenedicarboxylic acid (1, 2).

Ethylic pentane-$\omega_2\omega_4$-tetracarboxylate,

$(COOC_2H_5)_2CH{\cdot}(CH_2)_3{\cdot}CH(COOC_2H)_2$.

In order to prepare this substance, the following method has been found to give the best results:—

22 grams of sodium are dissolved in 250 grams of absolute alcohol, and when cool a mixture of 150 grams of ethylic malonate and 96 grams of trimethylene bromide are slowly added, care being taken that the temperature does not rise above 30°. On allowing this mixture to stand, a reaction soon sets in and is generally accompanied by evolution of heat sufficient to cause the alcohol to boil; as soon as this has subsided and the whole cooled down again, the decomposition is generally finished. On adding water and a few drops of dilute sulphuric acid, an oil is precipitated which is separated from the aqueous solution by extraction with ether. The ether is then distilled off and the residue subjected to a rapid distillation in a current of steam, as long as oily drops come over with the condensed water.

In this way, any unchanged trimethylene bromide and ethylic malonate, as well as the ethylic tetramethylenedicarboxylate formed in the reaction, are almost completely separated from the ethylic pentanetetracarboxylate, which at the end of the operation remains behind in the retort as a thick oily mass. This is next extracted with ether, the ethereal solution washed with a little dilute sodic carbonate, dried over calcic chloride, and the ether distilled off.

The residue, which is a slightly yellowish oil, usually weighing about 70 grams, is then further purified by fractioning under reduced pressure (100 mm.). By the first distillation nearly the whole distils over between 220° and 300°, and after repeated fractioning an oil is obtained boiling constantly at 259—262° (100 mm.). The analysis gave the following results:—

I. 0·1706 gram substance gave 0·3529 gram CO_2 and 0·1200 gram H_2O.

II. 0·1525 gram substance gave 0·3166 gram CO_2 and 0·1068 gram H_2O.

	Theory.	Found.	
$(COOC_2H_5)_2CH\cdot(CH_2)_3\cdot CH(COOC_2H_5)_2$.		I.	II.
C......	56·67 per cent.	56·42	56·62 per cent.
H.....	7·78 „	7·81	7·78 „
O.....	35·55 „	35·77	35·60 „

Ethylic pentane-$\omega_2\omega_2$-tetracarboxylate is a thick, colourless oil, which does not solidify at 0°. When quite pure, it can be distilled under ordinary pressure, with only very slight decomposition.

Pentane-$\omega_2\omega_2$-tetracarboxylic Acid and Pimelic Acid,
$COOH\cdot(CH_2)_5\cdot COOH$.

The next step was to endeavour to obtain from this ethereal salt the free pentanetetracarboxylic acid, and from this, pimelic acid by the splitting off of carbonic anhydride. For this purpose, 10 grams of the pure ethereal salt was mixed with an alcoholic solution of potash (containing 10 grams of KOH), and after the violence of the reaction had subsided, the whole was heated with a reflux condenser for six hours to boiling, at the end of which time hydrolysis was complete. In order to isolate the product, water was now added and the clear solution evaporated almost to dryness on a water-bath. The residue was then mixed with an excess of dilute sulphuric acid, and extracted at least 20 times with pure ether.

This ethereal solution, after drying over calcic chloride and evaporating, deposited a slightly brownish-coloured oily acid, which is probably pentanetetracarboxylic acid, as it is easily decomposed on heating into 2 mols. CO_2 and pimelic acid, as shown in the introduction. This change is best effected by heating the crude tetracarboxylic acid in an oil or metal bath at 200° until the evolution of carbonic anhydride ceases, and then dissolving the residue in water. This solution is then filtered from a small quantity of insoluble resinous matter, and extracted five or six times with pure ether. The ethereal solution after drying and evaporating, deposits the crude pimelic acid as a nearly colourless oil, which solidifies almost completely on standing for some days over sulphuric acid in a vacuum. This crude substance was first roughly purified by spreading out on a porous plate and then recrystallised from water. The following results were obtained on analysis :—

0·1002 gram substance gave 0·2100 gram CO_2 and 0·0730 gram H_2O.

	Theory. $COOH·(CH_2)_5·COOH$.	Found.
C........	52·50 per cent.	52·44 per cent.
H........	7·50 „	7·52 „
O........	40·00 „	40·04 „

This acid melts at 100—102°, and is undoubtedly identical with the pimelic acid obtained by Baeyer (*Ber.*, **10**, 1358) by the reduction of furonic acid with hydriodic acid and phosphorus. Schorlemmer and Dale (*Annalen*, **119**, 147) also prepared the same acid by the oxidation of suberone with concentrated nitric acid.

Disodic Derivative of Ethylic Pentanetetracarboxylate, $(COOC_2H_5)_2CNa·(CH_2)_3·CNa(COOC_2H_5)_2$.

If ethylic pentanetetracarboxylate,

$$(COOC_2H_5)_2CH·(CH_2)_3CH(COOC_2H_5)_2,$$

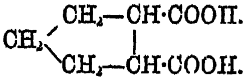
is treated with excess of sodic ethylate, the two hydrogen-atoms of the CH-groups are displaced by sodium, forming the disodium compound, $(COOC_2H_5)CNa·(CH_2)_3CNa(COOC_2H_5)_2$. In order to prepare this substance for analysis, a weighed quantity of ethylic pentanetetracarboxylate was dissolved in a little pure ether and mixed with an ethereal solution of sodic ethylate (2 mols.). The clear solution soon begins to deposit the disodic compound, and in a short time the whole becomes filled with a thick white precipitate. This is quickly collected, washed once or twice with a mixture of 1 pt. alcohol and 2 pts. ether and dried over sulphuric acid in a vacuum. Analysis :—

0·3754 gram substance gave 0·1364 gram Na_2SO_4.

	Found.	Theory. $C_{17}H_{26}O_8Na_2$.
Na	11·76 per cent.	11·38 per cent.

This disodic compound is a white apparently amorphous powder, which is very easily soluble in water. On the addition of an acid, it is at once decomposed, an oil being precipitated which is probably regenerated ethylic pentanetetracarboxylate.

Pentamethylenedicarboxylic Acid (1, 2),



The disodium compound of ethylic pentane-$\omega_2\omega_3$-tetracarboxylate when treated with bromine is converted quantitatively into ethylic pentamethylenetetracarboxylate, as shown in the introduction. In carrying out this synthesis, the following method has been found to give the best results:—

18 grams of ethylic pentanetetracarboxylate are dissolved in about 50 grams of pure dry ether, and then an ethereal solution (this vol., p. 21) of sodic ethylate, containing 2·3 grams of sodium is slowly poured in, both ingredients being carefully cooled before mixing. After standing for about a minute to allow the sodium compound to separate out, 8 grams of dry bromine are added slowly through a dropping funnel, the mixture being well agitated and cooled during the operation. The colour of the bromine disappears instantly on coming in contact with the sodium compound, but the last drop should impart to the solution a pale yellow tint. As soon as all the bromine has been added, the product is allowed to stand for about an hour, then mixed with an equal volume of water, and the ethereal layer separated from the aqueous solution by means of a separating funnel.

After once washing with water and distilling off the ether, an almost colourless oil is obtained, which is crude ethylic pentamethylenetetracarboxylate. This was not analysed, but converted directly into the free acid by hydrolysis, and this then into the pentamethylenedicarboxylic acid (1, 2), which, as it is a beautifully crystalline substance, could easily be obtained pure for analysis. For this purpose, the crude ethylic pentamethylenetetracarboxylate was mixed with a solution of 15 grams of pure potash dissolved in a little alcohol, and heated for six hours to boiling on a water-bath. The mass was then dissolved in water, evaporated to expel the alcohol, the residue treated with an excess of dilute sulphuric acid, and extracted at least 20 times with pure ether.*

The ethereal solution is now very carefully dried over calcic chloride, filtered, and the ether distilled off, when the crude pentamethylenetetracarboxylic acid remains behind as a thick brownish syrup To convert this into the dicarboxylic acid, it is now heated at 200—220° until the evolution of carbonic anhydride ceases, which is usually the case in about half an hour. The crude residue can then be purified by dissolving it in water and decolorising with animal charcoal, as described in the *Berichte* (18, 3250); the following method, however, has since been found to give better results.

---

* Or the acid may be isolated by means of the lead salt, as described under "Tetramethylenetetracarboxylic Acid" (this vol., p. 22). This method is, however, not to be recommended if large quantities are operated on, as the lead salt is very difficult to filter and wash well.

The impure substance is mixed with about three times its volume of absolute alcohol, thoroughly saturated with hydrogen chloride, and allowed to stand for three or four hours. Water is then added, and the whole extracted two or three times with ether. The ethereal solution is well washed with sodic carbonate solution, dried over carbonate of potash, and the ether distilled off. The residue is crude ethylic pentamethylenedicarboxylate. This is first roughly purified by distillation under reduced pressure (200 mm.), and then by fractionation under ordinary pressure.

After two fractionings, by far the greater part distils over between 245° and 255°. A sample of ethylic pentamethylenedicarboxylate boiling at 249—252° gave the following results on analysis:—

0·1370 gram substance gave 0·3090 gram CO_2 and 0·1043 gram H_2O.

	Calculated for $C_5H_8(COOC_2H_5)_2$.	Found.
C........	61·68 per cent.	61·51 per cent.
H	8·41 „	8·46 „
O........	29·90 „	30·03 „

Ethylic pentamethylenedicarboxylate (1, 2) is a colourless oil of disagreeable odour.

In preparing free pentamethylenedicarboxylic acid it is not necessary to use the pure ethylic salt; the fraction boiling at 245—255° was found to answer equally well. The hydrolysis was carried out as usual, by boiling the ethereal salt with a slight excess of alcoholic potash for three hours on a water-bath, and then evaporating to dryness. The residue was dissolved in a small quantity of water, acidified with dilute sulphuric acid, and allowed to stand in a cool place for 24 hours.

At the end of this time, the acid had almost entirely crystallised out, forming a hard cake at the bottom of the beaker; this was collected, washed with water, and recrystallised twice from water. It was thus obtained in curious nodular masses, which, after drying at 100°, gave the following numbers on analysis:—

I. 0·1750 gram substance gave 0·1004 gram H_2O and 0·3410 gram CO_2.

II. 0·1508 gram substance gave 0·0874 gram H_2O and 0·2941 gram CO_2.

III. 0·2318 gram substance gave 0·1330 gram H_2O and 0·4484 gram CO_2.

	Theory.	Found.			
	$C_5H_8(COOH)_2$.	I.	II.	III.	
C....	53·16 per cent.	53·14	53·19	53·15	per cent.
H....	6·33 „	6·37	6·43	6·33	„
O....	40·51 „	40·49	40·38	40·52	„

Pentamethylenedicarboxylic acid (1, 2) melts at 160°. It is easily soluble in hot water, alcohol, and ethyl acetate, sparingly in cold water, ether, benzene, chloroform, and light petroleum.

The silver salt was prepared by precipitating the neutral solution of the ammonium salt with silver nitrate. It is a heavy, white, apparently amorphous precipitate, almost insoluble in water. For analysis, it was dried over sulphuric acid in a vacuum.

I. 0·2551 gram substance gave 0·0501 gram H_2O, 0·2096 gram CO_2, and 0·1473 gram Ag.
II. 0·1812 gram substance gave 0·1050 gram Ag.

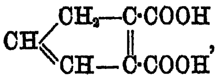
	Theory.	Found.	
	$C_5H_8(COOAg)_2$.	I.	II.
C	22·58 per cent.	22·41	—
H	2·15 „	2·17	—
Ag	58·07 „	57·74	57·94 per cent.

On adding cupric sulphate to a neutral solution of the ammonium salt of pentamethylenedicarboxylic acid, the *copper* salt is precipitated as a beautiful green amorphous mass, which is sparingly soluble in water.

Plumbic acetate gives with a cold solution of the ammonium salt a white amorphous precipitate. If, however, the solutions are mixed boiling, the lead salt is precipitated as a white crystalline mass. This, on examining it with a microscope, is found to consist of transparent plates, grouped together like rosettes.

The most characteristic salt of pentamethylenedicarboxylic acid is the *calcium salt*. If calcic chloride solution is added to the cold solution of the ammonium salt, no precipitate is formed; on heating slowly to boiling, however, a colourless crystalline precipitate gradually separates out, which does not redissolve on cooling. This precipitate, when examined under the microscope, is found to consist of a mass of perfectly formed octahedrons, interspersed with examples of the combination O . ∞O∞. In these latter the surfaces ∞O∞ are very small, but very clearly defined, and easily seen when examined with a fairly high power. This precipitate is remarkable as consisting only of single crystals, each of which is perfectly formed.

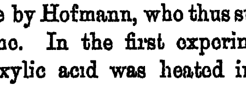
Several experiments have been made with the object of obtaining a compound of the formula—



by removing 4 hydrogen-atoms from pentamethylenedicarboxylic acid, but as yet without result. Oxidising agents split up this acid completely, oxalic acid being formed.

The action of bromine on pentamethylenedicarboxylic acid was therefore studied, as it was thought that in this way better results might be obtained, more especially as similar experiments to these have already been made by Hofmann, who thus succeeded in converting piperidine into pyridine. In the first experiment, 1 gram of pure pentamethylenedicarboxylic acid was heated in a sealed tube with 2 grams of bromine for two hours at 100°. On taking out the tube, no change was perceptible, and the same was the case after heating for two hours at 150°, but on heating at 180° for four hours the acid was completely decomposed, abundance of hydrogen bromide being formed and a mass of charcoal being left behind in the tube. In experiment II, the same quantities were used, the only difference being that the acid was first dissolved in a small quantity of water. In this case, also no action took place until a comparatively high temperature had been reached, when total decomposition into hydrogen bromide and charcoal took place. It is hoped that by changing the conditions in the above experiment, better results may be obtained.

Anhydride of Pentamethylenedicarboxylic Acid, 1, 2,



Pentamethylenedicarboxylic acid is an extremely stable compound which, if rapidly heated, can be distilled in small quantities almost without decomposition. If, however, it be kept at a temperature of 300°, it gradually loses water and is converted into its anhydride. In order to prepare this substance for analysis, 2 grams of the pure acid were heated in a very small retort at 300° for half an hour, and the product then distilled as rapidly as possible over the naked flame. In this way an almost colourless oil condensed in the neck of the retort, which, on cooling, completely solidified to a hard crystalline mass. This was carefully ground in an agate mortar, washed with small quantities of ether, and dried first on a porous plate and then over sulphuric acid in a vacuum. The following numbers were obtained on analysis:—

I. 0·1567 gram substance gave 0·0809 gram H_2O and 0·3438 gram CO_2.

II. 0·1700 gram substance gave 0·0871 gram H_2O and 0·3716 gram CO_2.

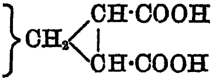
Theory.	$C_7H_8O_3$.	Found. I.	Found. II.
C	60·00 per cent.	59·83	59·61 per cent.
H	5·71 „	5·73	5·69 „
O	34·29 „	34·44	34·70 „

The anhydride of pentamethylenedicarboxylic acid thus prepared melts at 64—67°. It is fairly easily soluble in ether, benzene, chloroform, and alcohol, but only sparingly in light petroleum and bisulphide of carbon. It is almost insoluble in carbonate of soda solution at ordinary temperatures, but is more rapidly converted into the acid on heating.

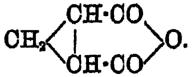
If this anhydride is warmed with resorcinol and a few drops of sulphuric acid, and the melt treated with ammonia, a most beautifully fluorescing solution is produced.

Pentamethylenedicarboxylic acid and its anhydride form the third member in the series of orthodicarboxylic acids of closed carbon-chains which have been obtained synthetically, thus:—

Trimethylenedicarboxylic acid (1, 2)* ....

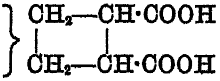


(M. p. 137°).

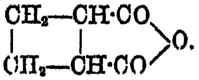


Anhyd. (m. p. 57°).

Tetramethylenedicarboxylic acid (1, 2)† ....

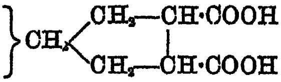


(M. p. 130°).

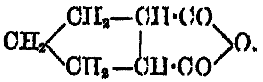


Anhyd. (m. p. 76—78°).

Pentamethylenedicarboxylic acid (1, 2) ....



(M. p. 160°).



Anhyd. (m. p. 64—67°).

---

* Conrad Guthzeit, *Ber.*, 17, 1185.

† This vol., pp. 22—25.

XXVII.—*Absorption of Gases by Carbon.*

By Charles J. Baker, B.A., Demonstrator of Chemistry, University Museum, Oxford.

Although the extent to which charcoal absorbs various gases and vapours has been thoroughly examined, notably by J. Hunter (*Jour. Chem. Soc.*, 1865, 285; 1867, 160; 1868, 186; and *Phil. Mag.* [4], **25**, and **29**), yet the composition of the gas obtained on attempting to remove them by the application of heat has been but little studied. In an abstract of a paper by Angus Smith (*Proc. Roy. Soc.*, 1863, 424), it is stated that when it is sought to remove by the agency of heat the oxygen absorbed by charcoal, carbon dioxide is obtained. Reichardt (*J. pr. Chem.*, **98**, 418), while noting the same fact, also observed that the quantity of gas that could be expelled by heat varied with the degree of moisture. In this paper experiments are described, which were undertaken with the object of ascertaining the nature of the gases produced on heating carbon which has absorbed oxygen, the tubes in which the absorption was conducted being exhausted by the mercury pump before the heating was commenced.

It was determined to examine the nature of the gases evolved when carbon which had absorbed oxygen was subsequently heated to various temperatures.

1. To 0°.
2. To the ordinary temperature of the atmosphere.
3. To 100°.
4. To temperatures above 100°.

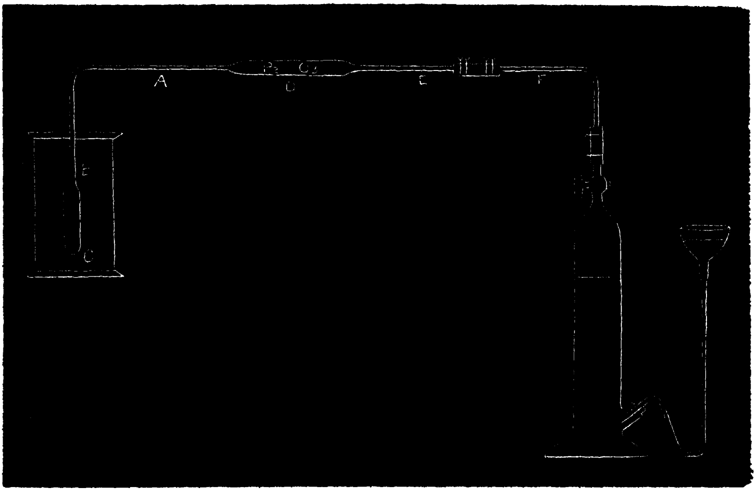
The temperature of absorption in the first three cases was considerably below zero, and in the fourth case was at 12°. In view also of the fact that the presence of moisture has an influence on the extent to which carbon undergoes combustion in an atmosphere of oxygen (H. Brereton Baker, Trans., 1885, p. 349), it was resolved to conduct the experiments, when desirable, in duplicate; in one series the absorbed oxygen was dried, and in the second series, saturated with moisture.

Mode of Experimenting.

Each experiment may be considered as having been performed in two stages. First, into a hard glass tube sealed at one end and drawn out at the other to the diameter of a quill, a quantity of purified carbon was introduced. By means to be subsequently described, the carbon and the tube were freed from absorbed and free gases and moisture as far as possible, and the tubes sealed. The vacuous tube containing the carbon was then opened in the particular gas that was to be absorbed, the time, temperature, and pressure under which absorption took place being noted. After exhausting the tube of all gas not retained by the carbon, it was sealed. Secondly, the tube, now containing the carbon and the gas absorbed within it, was heated, and at the end of a noted time it was exhausted of any gas that had been given out by the carbon, the temperature being kept constant till the exhaustion was complete. The gas obtained was collected, analysed, and the percentage composition calculated.

The more important details of the experiment are as follows:—Well cleansed pieces of the hardest glass tubing from one-quarter to one-third of an inch in internal diameter, were sealed at one end, C (see p. 251), and at a distance of about 2½ inches drawn out into a quill tube. Plugs of phosphorus pentoxide occupied some two or three inches of the tube at D; finally, the tube was drawn out to E. In order to introduce the carbon into C the tube was cut at B. Before sealing on again at B the piece of tubing now containing carbon, the upper part of C was heated in order to burn away any adhering carbon. It will be obvious that the whole of the carbon should be concentrated at one point. To remove the air and moisture from the tube and carbon, the end E was attached to a Sprengel pump, and then the end C was heated to the highest temperature of the Bunsen flame. This heat was maintained for half an hour after the last trace of gas had been given off. The temperature to which the carbon was thus raised was very much higher than that to which it was subsequently subjected. It was attempted to remove the last trace of moisture by heating the carbon at 150—200° for three or four days. A set of tubes of this form, sealed off at E, was prepared and employed for the absorption of dried gases. Another set prepared in a similar manner, except that the last traces of moisture were allowed to remain, was used for the absorption of moist gases, the tubes being sealed at E vacuous.

The absorption itself was conducted in the following manner. In the first place it will be well to describe the way in which the process was carried out when no moisture was present. The particular gas, dried by passing over phosphorus pentoxide, was collected in a gas pipette. The carbon tube CDE was attached to the pipette by means of caoutchouc and glass tubing (as shown in the figure). Before, however, the end E was introduced into the caoutchouc connection, gas was allowed to drive out air and fill the parts above the tap. The caoutchouc joinings were wired on and covered with melted paraffin. The end E, lastly, was broken and the tap partially, afterwards fully, turned on. Thus the exhausted and dried carbon was brought into contact with the dry gas. The carbon was allowed to remain in contact with the gas for a time far in excess of that during which any absorption could be observed to take place. The pressure of the gas was readily preserved at 760 mm. by raising or lowering the mercury reservoir, according as the barometer stood below or above this point. The part of the tube marked CB remained in a vessel of water, or a freezing mixture, according as the absorption was to take place at the ordinary temperature, or below zero. The time for absorption having elapsed, the tube was sealed near E and exhausted by a Sprengel pump of all gas not retained by the carbon. Tubes thus prepared were then heated in the way to be subsequently described.



If the experiment was to be made with moist instead of dry carbon, the method of working adopted was very similar. The carbon tube, however, was of the form ABC, and before attachment to the caoutchouc a globule of water was introduced into the glass tube about some point F. When the end A had been broken, and the tap turned on, the water was gently heated and became condensed in proximity to the carbon.

Of the materials employed little need be said. As regards the carbon, that from boxwood and animal charcoal was selected. The initial experiments were made with boxwood charcoal, but from the small volume of gas obtained on exhaustion compared with that from animal charcoal, the latter was used throughout. It was purified as follows:—The finely divided charcoal was digested repeatedly with hydrochloric acid, and washed by decantation. When found to be quite free from phosphate, a quantity was ignited at a strong heat, in a furnace, in a current of chlorine for some eight hours. To free the carbon from at any rate the greater part of the chlorine, it was gently warmed in the air, then boiled with hydrochloric acid to remove the bases present, and subsequently introduced into a tube of the shape shown in the figure, short sticks of potassium hydrate being placed at D. After being strongly heated in a vacuum, the last traces of chlorine were removed, and a stock of purified carbon thus obtained.

Pure oxygen and carbon dioxide were prepared in the usual manner: the one from recrystallised potassium chlorate, and the other from calcspar.

If an experiment with a dry gas was to be made, the gas was passed through sulphuric acid and over phosphorus pentoxide, and stored in gas pipettes over mercury.

In experiments with moist gases, these were collected directly in gas pipettes after washing with water. In each case the gas was analysed before use, and its purity assured.

Exhaustion of Carbon which had absorbed Oxygen at −15°, *the Temperature being subsequently raised to* 0°.

Two of the prepared tubes containing carbon, exhausted and in a vacuum, were opened in contact with moist oxygen from the pipette. The end of the tube containing the carbon was immersed in a freezing mixture, the temperature not being allowed to rise above −15° during the hour that the carbon and oxygen were in contact. The carbon was shaken up at times to ensure the absorption being as complete as possible. At the end of the hour, the caoutchouc connection was firmly clamped and attached to the mercury pump. The latter having been freed from air the clamp was opened, and the unabsorbed oxygen removed from above the carbon. The tube was now sealed off and the temperature of the carbon which had remained at −15° during exhaustion was raised to 0°. After remaining for an hour at this point, the tube was opened in connection with a vacuous Sprengel pump, when it was found that no gas had been given up by the carbon. It had been thought that the temperature might be too low for the combination, and that free oxygen would be evolved. The result obtained is of some interest taken in conjunction with subsequent deductions.

The two tubes were again sealed and allowed to rise in temperature to that of the atmosphere, at which they were kept for three months;

at the end of this time they were found still to be vacuous. After a further period of three months, it was ascertained that even then the carbon had not evolved any gas.

Absorption of (i) *Oxygen and Water Vapour;* (ii) *of Oxygen;* (iii) *of Water Vapour, and subsequent Exhaustion at* 100°.

It was from the results of preliminary experiments that the investigation of the absorption of more or less dried oxygen and exhaustion at 100° took the form indicated above. It was determined to examine the composition of the gases found on exhaustion of carbon which has absorbed—

i. Oxygen saturated with moisture.
ii. Oxygen freed as far as possible from moisture.
iii. Water vapour alone.

(i.) Three of the sealed tubes of the form ABC were taken containing about one, two, and three grams of exhausted carbon respectively. After having been connected with the gas pipette, the end containing the carbon was introduced into a freezing mixture, the temperature of which was below —12°. After a short time, the end A was broken, and oxygen saturated with moisture was admitted. The absorption was apparently completed after the lapse of a few minutes: nevertheless, it was allowed to continue for an hour. The caoutchouc connection of A was next tightly clamped, and the tube still resting in the freezing mixture was exhausted and sealed at —12°. The temperature had been maintained during absorption as nearly as possible at this point. The gas thus obtained on exhaustion was analysed, but no carbon monoxide or dioxide was present. It was simply pure oxygen.

The tube was next placed in a water-bath and kept at 100° for seven days; it was then exhausted at this temperature. The weight of the carbon employed was ascertained in each case, and from the sp. gr. (which was specially determined, and in the case of the animal charcoal used was found to be 1·64) the volume was calculated. From the tabulated results (p. 254), it will be seen that under the conditions of the experiment carbon yields on exhaustion at 100° nearly seven times its volume of carbon dioxide.

(ii.) Three tubes were treated in a manner similar to the above, dry oxygen being employed instead of the moist gas. It was found that the tubes after seven days' digestion at 100° remained vacuous.

(iii.) In order to ascertain whether water vapour digested with carbon at 100° for seven days would give rise to the production of any free oxide or oxides of carbon, three tubes were prepared con-

Exhaustion of Absorbed Oxygen from Carbon at 100°.

Gas absorbed.		Temp	Pressure.	Duration.	Temp.	Duration	Vol of gas evolved in c.c.	Vol. of carbon.	Ratio of vol. of gas evolved to carbon used.	
		Of absorption.			Of heating.					
Oxygen saturated with water	1	– 12	760	1 hour	100°	7 days	5·2 CO_2	0·732	7·10	6·96 (mean)
	2	„	„	„	„	„	9·68 CO_2	1·41	6·86	
	3	„	„	„	„	„	13·99 CO_2	2·02	6·92	
Oxygen	4, 5, 6	„	„	„	„	„	nil	1·5+		
Water.........................	7, 8, 9	„	„	„	„	„	nil	1·5+		

taining about 2 grams of carbon each, and a drop of water in the drawn-out part used for connecting with the Sprengel pump. After strong ignition to remove absorbed gases, the tubes were sealed. The water was evaporated by heat, and brought in the vaporous state in contact with the carbon. On exhaustion after a lapse of seven days no carbon monoxide or dioxide was found. The tubes contained water vapour only.

These results show the extent to which carbon combines with moist oxygen absorbed within it, and also indicate the influence which water has in bringing about the combination.

Further, it is seen that when the attempt is made to remove moist oxygen, absorbed in carbon at —12°, and held by it after the experimental tube is rendered vacuous, by raising the temperature to 100°, carbon dioxide is produced. If dry, no free gas is obtained.

It may be added that when the oxygen is neither specially dry nor specially moist and the temperature raised to a dull red heat, no oxygen was obtained on exhaustion, but a mixture of carbon monoxide and dioxide.

Exhaustion of Absorbed dried Oxygen from dried Carbon.

It has already been seen that on attempting to remove the dried oxygen retained by carbon by a digestion extending over seven days at 100°, no gas was obtained. This suggested the point as to whether in the first place dried oxygen is absorbed by dried carbon at all; and in the second place, if absorption does take place, whether on raising the temperature the absorbed gas would be given up as oxygen, as carbon monoxide, or as carbon dioxide.

Five of the tubes specially prepared for the absorption of dried gases and containing dried carbon were allowed to absorb dry oxygen at 12°. After exhausting at this temperature, the tubes were sealed. In order to remove the last traces of moisture, the parts of the tubes containing carbon were heated in air-baths at about 150° for a week. Two of the number were further set apart for two months in a place having a temperature of 35—40°. One of the remaining three tubes was now attached to a vacuous Sprengel pump and opened in connection with it. Only a trace of carbon dioxide was obtained. The temperature was raised to 350° by stages of 50° at a time, but still only traces of carbon monoxide and dioxide were produced. The time during which the applications of heat extended lasted from 25 hours to two days. The small bubbles of gas, when obtained, were always produced immediately on raising the temperature.

On raising the temperature to 450°, however, a slow but regular evolution of gas took place; the heating was continued for two hours.

The temperature of 450° was estimated by simultaneously heating comparison tubes containing salts of known melting points. Silver chloride (fusion point 451°) was melted by the heat required for the evolution of the absorbed gas. When the evolution had ceased, the carbon was raised to full redness, but no more gas was given out. Nearly 5 c.c. of gas were thus obtained for analysis; the traces of carbon monoxide and carbon dioxide produced by the gradual increase of temperature amounted only to 0·2 c.c.

The two remaining tubes of this set of three were then raised in temperature to about 450°, and evolved gas. The analysis showed that carbon monoxide was the main constituent and that no free oxygen was evolved.

The two tubes which had remained at 35—40° for two months were examined, but one failed. On exhausting at about 450°, it showed that the oxygen had almost entirely combined with the carbon to produce carbon monoxide (this is marked 1 on the table).

Exhaustion of dried Oxygen from dried Carbon.

Dried for		Time of absorption.	Temp.	Pressure.	Temp. of exhaustion.	Percentage obtained of		
			Of absorption.			CO.	CO$_2$.	
2 months..	1	10 hours	12°	760	450°	98·91	1·08	About 0·6 c.c. of carbon used.
1 week....	2	,,	,,	,,	,,	88·65	11·28	
1 week....	3	,,	,,	,,	,,	82·76	17·2	
1 week....	4	,,	,,	,,	,,	76·29	23·7	

The results taken as a whole indicate that absorbed dried oxygen can only be removed from dried carbon as carbon monoxide by the application of heat. It would, however, be a premature assumption to state that the carbon had been directly burned by the oxygen to carbon monoxide. It is within the range of possibility that carbon dioxide is first produced, and that in passing over and through the heated carbon it is reduced to monoxide. To ascertain whether this is the case, it was only necessary to repeat the above experiments, employing dried carbon dioxide for absorption instead of oxygen.

Exhaustion of dried Carbon Dioxide from dried Carbon.

Four tubes containing exhausted dried carbon in a vacuum, and with the phosphorus pentoxide tube attached, were allowed to absorb dried carbon dioxide and then sealed. In order to remove moisture, the carbon in two of the tubes was heated at about 150° in an air-bath for seven days; two were heated for three days. They were then allowed to cool to 12°, and left at this temperature for some three hours in order that the carbon dioxide might again be taken up by the carbon. After removing any unabsorbed carbon dioxide the carbon was raised in each tube to 450°, and the gases evolved collected by the mercury-pump, and analysed. These are the results:—

Dried for	Duration of absorption.	Temp	Pressure	Temp. of heating.	Percentage obtained of	
		Of absorption.			CO_2	CO.
1 week	1 hour	12°	760	about 450°	76·3	23·6
1 week	"	"	"	"	74·1	25·8
3 days	"	"	"	"	52·7	47·3
3 days	"	"	"	"	50.6	49·4

From the foregoing it will be observed that the drier the substances are the larger the proportion of carbon dioxide produced; or, to put it in another way, the less the reduction of carbon dioxide to monoxide. Hence, the dried oxygen retained by carbon, when removed by heating it at 450°, doubtless burns the carbon to monoxide direct.

Summary of Results.

The conclusions arrived at are—

1.—That moist oxygen which is absorbed and retained by carbon in a vacuum, the absorption being for an hour at −15°, is not given out either free or combined by raising the temperature to 0°; that, further, the same being raised in temperature to about 12°, and kept at that temperature even for prolonged periods, yields no free gas.

2.—(*α*.) That the water vapour and oxygen similarly absorbed, if kept at 100° for a week, give rise to the production of carbon dioxide only, the volume of gas obtained being nearly seven times the volume of the carbon employed.

(*β*.) Water vapour and carbon digested for a week at 100° produce no free carbon dioxide; and

(*γ*.) There is no production of free oxygen or oxide of carbon when carbon and oxygen freed from moisture are digested at the same temperature for the same time.

3.—(α.) That a temperature of 450° is required to remove the dried oxygen retained by carbon, and that carbon monoxide is the main product formed.

(β.) The more free from moisture the substances employed are, the less does the carbon burn in the carbon dioxide which it absorbs; and hence

(γ.) Carbon is burned directly to carbon monoxide by the absorbed and firmly retained oxygen.

XXVIII.—*An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds.*

By HENRY E. ARMSTRONG.

IT is well known that certain mono-derivatives of benzene yield a mixture of *para-* and *ortho-*di-derivative in proportions which apparently are much affected by the conditions under which substitution takes place, the *meta-*di-derivative being formed in relatively very small proportion, if at all; whereas other mono-derivatives chiefly yield the *meta-*di-derivative. A very noteworthy illustration of the manner in which the radicle first introduced exercises a specific influence on the subsequent displacement of a second hydrogen-atom is afforded by the production of a mixture of *ortho-* and *para-*nitrobromobenzene on nitrating bromobenzene, but of *meta*bromonitrobenzene on bromination of nitrobenzene in presence of ferric chloride (*Annalen*, **231**, 158). I am not aware that up to the present time any explanation of the remarkable difference in behaviour of mono-derivatives of benzene here referred to has been even hinted at.

To afford an opportunity of contrasting the behaviour of the various mono-derivatives of benzene, the accompanying tables (I and II) have been arranged, showing the nature of the radicle R′ contained in the mono-derivative and the position which the radicle X′ assumes relatively to R′. Whenever possible, the position of X′ in the chief product is indicated by printing the figure in thick type; the position which it assumes in the product which is obtained in very small amount is indicated by underlining the figure; where no distinction is made, it is either because the proportions vary with the conditions, or more often because exact information on this point is wanting. Table I illustrates what may be termed the para-ortho-law; Table II the meta-law.

TABLE I.—*Illustrating Para-ortho-law.*

R′.	Position of X′ relatively to R′.				
	Cl.	Br.	I.	NO_2	SO_3H.
CH_3	2, 4	2, 4, 3	—	2, 4, $\underline{3}$	2, 4
CH_2Cl	4	—	—	4	—
$CHCl_2$	4	—	—	3	—
CCl_3	4	—	—	3	—
Cl.	2, 4	2, 4	—	2, 4	4
Br	—	2, 4	—	2, 4	4
I	—	—	4	2, 4	4
OH	2, 4	2, 4, 3 (?)	2, 4, 3 (?)	2, 4	2, 4
NH·Ac	2, 4	2, 4	4	2, 4	—
$NH_2 \cdot SO_4H_2$	—	—	—	2, 4 $\underline{3}$	4
$CH_2 \cdot COOH$	2, 4	4	—	2, 4	—
CH CH·COOH	—	—	—	2, 4	—

TABLE II.—*Illustrating Meta-law.*

R′.	Position of X′ relatively to R′.				
	Cl	Br	I.	NO_2.	SO_3H.
NO_2	3	3	—	3, 2, 4	3, 2, 4
CN	—	—	—	3	—
COH	—	—	—	3	—
$CO \cdot CH_3$	—	—	—	3, 2	
$CO \cdot CH_2Br$	—	—	—	3	—
$CO \cdot C_6H_5$	—	—	—	—	4
CO·OH	3	3	3	3, 2, 4	3, 2, 4
$SO_2 \cdot OH$	—	3	—	3, 2, 4	3, 4
$SO_2 C_6H_5$	—	—	—	3	3

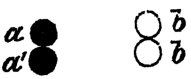
Now, on careful study of the examples collected in these tables, it will be noted that R′ in all compounds which obey the para-ortho-law is either a monad simple radicle or a compound radicle in which the grouping element of the radicle is combined with one or more monad radicles; whereas in compounds subservient to the meta-law the grouping element of the radicle R′ is associated with one or more polyad atoms—with N in CN, with O in NO_2, COH, $CO \cdot CH_3$ and

CO·OH. The double influence exercised by $CHCl_3$ and CCl_3 is remarkable.

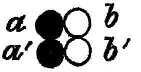
Before attempting to make use of these facts, it will be desirable to consider what conception is to be attached to the term "substitution"; in what way is substitution effected? Obviously, equations such as are commonly used—for example: $C_6H_6 + Br_2 = C_6H_5Br + HBr$—afford no information regarding the course of change, but serve merely to indicate the relative quantities concerned in the interaction; and text-books are all but silent on such matters. There would appear, however, to be floating in the minds of most of those who have been at the pains to consider this question at all a more or less clearly defined idea that in some way or other dissociation precedes substitution; that simplification is the antecedent of complication. Williamson, as far back as 1851, in his celebrated paper on the "Theory of Etherification," clearly expresses this view in words which leave no doubt (*Quart. Journ. Chem. Soc.*, 4, 110). To quote but a few of his sentences, he says: "We are thus forced to admit that in an aggregate of molecules of any compound there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united; but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course, this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place) . . . . . . the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper . . . . . . Thus it is that at any moment of time in which we examine the mixture, the bases are divided between the acids . . . . . . Such is the general process of chemical decomposition."

These views necessarily derived much support from the researches of Deville and his pupils on dissociation; and it can scarcely be doubted that their acceptance at the present day is mainly attributable to Deville's discoveries. The classical research which led to their conception cannot now be said to afford any very cogent argument either for or against them.

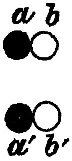
I have elsewhere ventured to express my doubts concerning the universal occurrence of dissociation in the case of "atomic" compounds, and will here only add that the more I consider the evidence the more I am led to think that our views on this subject need modification in not unimportant particulars. Be this as it may, my object now is to advocate the view that in the formation of substitution-products—in reactions of so-called double decomposition—an additive compound is first formed by the union of the interacting substances. The conviction that this is the case has grown upon me during several years past, although I cannot say in what it originated; looking up the question recently, however, I find that Kekulé in his *Lehrbuch der organischen Chemie* (Erlangen, 1867) takes this view in the most decided manner possible, speaking of it, in fact, as "Die einfachste und auf alle Fälle anwendbare Vorstellung;" he even goes so far as to express the idea graphically in the following manner:—



Before decomposition.



During decomposition.



After decomposition.

The two quotations serve to show that even authorities differ as to the interpretation which is to be given of the course of chemical change.

The formation of additive compounds has been observed in so many cases, that the possibility of their being formed from carbon compounds generally, excepting the paraffins, will scarcely be questioned, I imagine;* it is therefore permissible at once to pass to the consideration of the process involved in the production of the additive compound and its subsequent resolution into the substitution derivative.

To take the simplest case possible afforded by a benzenoid compound—the conversion of benzene into bromobenzene: according to the view advocated in this communication, the initial stage would be the addition of a molecule of bromine to *one* of the *six carbon-atoms;* the hydrogen-atom attached to this carbon-atom would thus find itself in the immediate presence of an element for which it has a strong affinity, and a very slight disturbance would lead to its separation with one of the atoms of bromine, whereupon the other bromine-atom would assume the place of the hydrogen-atom thus removed. A precisely similar explanation of the formation of mono-derivatives generally may be given. It is here supposed that the formation of the additive compound does not involve the separation and distribution of the bromine-atoms; this is not a necessary assumption, however: indeed it is well known that the first visible product of the action of bromine on anthracene and also on phenanthrene is a comparatively stable dibromide in which apparently the bromine-atoms are distributed, and it is therefore possible that similar compounds are formed in other cases but escape detection owing to their instability. But in the case of anthracene and phenanthrene it is easy to account for the formation of dibromides; the compound bearing a corresponding relation to the hydrocarbon is in the case of naphthalene a tetrabromide, and in the case of benzene a hexabromide: a tetrachloride, but not a tetrabromide, is actually producible from naphthalene, and a hexabromide and hexachloride of benzene are known, but there is no evidence of the production of intermediate compounds similar to these: so that it does not appear improbable that distribution only occurs when opportunity is given for complete saturation of the elements of the carbon ring. In connexion with this question, the experiments of Ador and Rilliet are of special interest (*Ber.*, 8, 1286). These chemists added a relatively small quantity of bromine to very carefully cooled benzene, and after well washing and drying the solution, submitted it to the action of zinc ethyl. The product was then oxidised; and they obtained benzoic, meta- and para-bromobenzoic, meta- and para-phthalic acids, but not a trace either of orthobromobenzoic or of phthalic acid. Unfortunately the oxidation was effected by means of chromic mixture by which ortho-compounds are known to be destroyed; otherwise these results would serve to place it beyond doubt that in the formation of the additive compound the bromine-atoms do not become separated and attached to contiguous carbon-atoms.*

---

* I may, perhaps, with advantage direct attention to Schramm's observations on the bromination of benzene (*Ber.*, 18, 607); to an important investigation on the chlorination of toluene by Seelig (*Annalen*, 237, 169); and to a paper by Istrati (*Ann. Chim. Phys.* [6], 6, 367).

Frequently it is advantageous, if not essential, to add a so-called carrier in order to effect the production of haloid derivatives; the use of iodine for this purpose was first made known by Hugo Müller, in 1862, but of late years many metallic chlorides have been found to possess the property of facilitating the displacement of hydrogen by chlorine and bromine to a much greater extent than iodine. According to a recent statement by Seelig (*Annalen*, 237, 169), if toluene cooled to 0° be saturated with chlorine and anhydrous ferric chloride be then added, a vigorous effervescence will at once take place owing to the escape of hydrogen chloride. It would therefore seem that the function of such "carriers" is to induce the separation of haloid hydride from the additive compound. This explanation of the action of "carriers" appears the more probable as it is now well known that metallic chlorides such as are used for the purpose combine more or less readily with hydrogen chloride, forming unstable chlorhydrides.*

---

* It may be suggested in explanation of Ador and Rilliet's results, that an additive compound of 2 mols of benzene with 2 mols. of bromine is formed; and that the carbon-atoms affected are relatively in para-position; that the zinc ethyl acts initially by inducing the withdrawal of HBr, the place of the H atom withdrawn being at once taken by ethyl; and that by a repetition of this process either a para- or a meta-derivative is formed according as the second hydrogen-atom withdrawn as HBr is para- or meta- relatively to that first displaced.

Passing now to the consideration of the formation of di-derivatives, I may at once point out that the difference under discussion in the behaviour of the two classes of mono-derivatives is, in my opinion, attributable to the different manner in which they form additive compounds. In the case of those which furnish the ortho- and para-derivative, it may be held that the additive compound results from the union of the reacting molecule with the carbon-atom to which the radicle R′ is attached.

The formation of an ortho-di-derivative from an additive compound thus constituted would appear to follow as a matter of course, involving as it does merely the separation and displacement of the hydrogen-atom attached to the carbon-atom contiguous to that with which the radicle R′ is associated; but as a matter of fact, although in some cases the ortho-derivative preponderates—Seelig states that about twice as much ortho- as para-chlorotoluene is formed on chlorinating toluene—in the majority of cases the para-derivative is the chief product. In order to account for the preponderating influence which apparently is exercised upon the para-position, more than one attempt has been made to devise a symbol for benzene in which the carbon-atoms relatively in para-positions are exhibited as in direct connexion (see especially Körner, this Journal); but these cannot be regarded as successful. Moreover if the influence which certain radicles exercise upon the para-position were held to necessitate the assumption of a direct connexion between carbon-atoms which are relatively in para-positions, the influence which certain other radicles exercise in causing the production of meta-derivatives must consistently be held in like manner to afford evidence of the existence of a direct connexion between carbon-atoms which are relatively in meta-positions. My own opinion is that there is no such connexion,† and that the production of para-derivatives must be regarded as the result of a kind of isomeric or intramolecular change, which probably takes place owing to the existence in closed chain compounds of a tendency to form symmetrical di-derivatives. An even simpler explanation of the formation of para-derivatives would be afforded by the assumption that the additive compound results from the union of the reacting molecule not with the carbon-atom to which the radicle R′ is attached but with that which occupies the para-position relatively to R′. For example, the

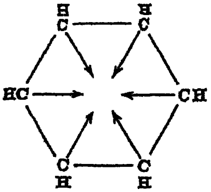
---

* The influence of iodine is probably ascribable to the readiness with which iodine chloride and bromide unite with other bodies.

† I may be allowed to quote here the following passage from a recent paper of mine on the "determination of the constitution of carbon compounds from thermochemical data" (*Phil. Mag.*, February, 1887:)—

"Thomsen . . . . maintains that the six atoms of carbon in this (benzene)

hydrocarbon are linked together by nine 'single bonds,' and not, in the manner indicated by Kekulé's well-known formula, by three single and three double bonds. Although of opinion that we cannot at present accept so absolute an interpretation of the thermochemical data, I yet think that Thomsen's results, taken together with all that is known of benzene, must be held to prove that benzene is in no sense a compound of the same order as an olefine; and that Kekulé's formula, if used at all, must be literally interpreted as indicating that the carbon-atoms are held together by nine affinities, there being abundant evidence to show that in the olefines the carbon-atoms are not held together by double bonds. In other words, if we employ Kekulé's benzene formula, we are bound to abandon the use of the conventional formula for olefines. From this point of view I see little difference between Kekulé's symbol and the prism formula or the modification of the latter quite recently advocated by Thomsen (*Ber.*, 19, 2944). Objections have, however, been urged against the prism formula which appear to be justified; the symbol advocated by Thomsen can scarcely be regarded as marking any particular advance; and Kekulé's symbol is open to the oft-raised objection that it indicates the existence of four distinct di-derivatives. I venture to think that a symbol free from all objections may be based on the assumption that of the twenty-four affinities of the six carbon-atoms twelve are engaged in the formation of the six-carbon ring and six in retaining the six hydrogen-atoms, in the manner ordinarily supposed; while the remaining six react upon each other,—acting towards a centre as it were, so that the 'affinity' may be said to be uniformly and symmetrically distributed. I would, in fact, make use of the following symbol:—



The only difference between this symbol and those employed hitherto arises from the fact that I do not consider that, apart from its connexion with the other carbon-atoms owing to their association in a ring, any one carbon-atom is directly connected with any other atom not contiguous to it in the ring; my opinion being that each individual carbon-atom exercises an influence upon each and every other carbon-atom." It should be added that this symbol is not directly applicable to benzene-derivatives. The introduction of a radicle doubtless involves an altered distribution of the "affinity," much as the distribution of the electric charge in a body is altered by bringing it near to another body.

observation that potassium phenyl *sulphate*, on heating, becomes potassium phenol *parasulphonate* (Baumann), or that the nitrosamine $C_6H_5{\cdot}NMe(NO)$ is converted by digestion with an alcoholic solution of hydrogen chloride into *paranitroso*methylaniline (*Ber.*, **19**, 2991), is sufficient to show that such an assumption is not necessary, however.

It remains but to add that there is abundant evidence to show that the proportions in which the para- and ortho-derivative are formed depend both on the nature of the reacting substances and the conditions at the time of change. Thus on heating *sodium* phenyl carbonate, sodium salicylate is formed, but *potassium* phenyl carbonate yields potassium parhydroxybenzoate; and whereas, according to Rosenstiehl, paranitrotoluene is the main product when a large excess of acid is used to nitrate toluene and the temperature is relatively high, orthonitrotoluene is chiefly formed if a small proportion of acid be used at a low temperature. In the case of phenol, however, Korner states that paranitrophenol is the chief product of nitration at a low temperature, and that orthonitrophenol is formed in larger quantity if the action takes place at higher temperatures.

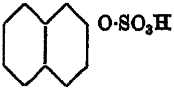
Attention has already been directed to the difference between the radicle R′ in compounds which obey the para-ortho-law and in those which obey the meta-law. Now it is to be noted that radicles such as CN, NO_2, CO, SO_2, the presence of which favours the production of meta-derivatives, are admittedly capable of uniting with a variety of compounds, the explanation usually given being that combination takes place owing to the conversion, by the addition of the elements of the molecule X′ Y′, of the radicle AB—in which both constituents are polyad atoms—into the group $A\left\{\begin{matrix}X'\\(BY)'\end{matrix}\right.$. Be this as it may, the radicles in questions are essentially different both in constitution and function from those whose presence favours the formation of ortho- and para-derivatives. Herein, I would suggest, lies the explanation of the meta-law, my opinion being that the additive compound which generates the meta-derivative is formed by the combination of the reacting molecule *with the radicle R′* of the mono-derivative, and not with the carbon-atom which carries that radicle.

Why an additive compound thus constituted should yield a meta- instead of an ortho- or para-derivative is a question to which no sufficient answer can be given at present; and we cannot hope to solve such a problem until the dynamics of the changes involved in the production of isomers have been thoroughly investigated. It is conceivable that the side-chain produced by the addition of the reacting molecule to the radicle R′ extends outwards sufficiently far to bring the added molecule into intimate connection with the carbon-atom and its associated hydrogen-atom in the meta-position; the conception is a purely mechanical one, but I do not think this a sufficient reason to reject it altogether from consideration, the tendency of modern investigation being to show that the occurrence of a particular change more often than not depends on the formation of a system of a particular configuration, as in the production of the lactones, for example. The formation of a *para*chloro-, but of a *meta*nitro-derivative from benzal chloride and benzotrichloride would appear to favour this explanation.

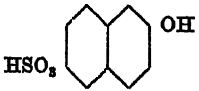
The production of a small proportion of meta-di-derivative from mono-derivatives which in the main obey the para-ortho-law may be accounted for by the assumption that the radicle R′ in these has also the power of combining with the reacting molecule; and it is noteworthy that the production of the meta-derivative appears to take place especially in those cases in which R′ contains a polyad atom; thus chloro- and bromo-benzene do not appear to furnish any meta-derivative, but a small proportion of meta-nitrotoluene is formed on nitrating toluene, and phenol is said to yield meta-bromo- and metiodo-phenol; and it is to be remarked that whereas acetanilide furnishes only the ortho- and para-derivative on nitration, aniline sulphate yields a small amount of meta-nitraniline also (Hübner).

In addition to the examples of compounds which obey the para-ortho- and meta-laws respectively given in Tables I and II, there are many others which are in complete agreement with them. So far as I am aware, there are only two apparent exceptions to be noted: the production of metaxylene from toluene and methyl chloride in presence of aluminium chloride, and the formation of a *para*sulphonic acid from benzophenone (Staedel). With regard to the former, although metaxylene is the chief product of the reaction in question according to Ador and Rilliet, it has since been stated by Jacobsen that orthoxylene is produced in by far the largest proportion; with regard to the latter, the exception is an interesting one, and it will be important to inquire into it, and to further study the behaviour of benzophenone.

The foregoing remarks have direct reference to benzene-derivatives proper; but it is desirable also to briefly point out that the consideration of the behaviour of benzenoid hydrocarbons generally is of the highest importance in any attempt to solve the problem involved even in the case of benzene itself. In a recent report to the British Association (comp. *Chem. News*, **54**, 326), I have summarised the results hitherto obtained by investigators of naphthalene-derivatives, and have especially dwelt on the fact that the preponderating tendency is to form α-derivatives; now this meets with an explanation on the assumption that an additive compound is first formed. According to my view, the carbon-atoms common to the two nuclei are centres of attraction, and the additive compounds result from the attachment of the reacting molecule to one or other of these; the formation of an α-derivative from an additive compound thus constituted would appear to be almost a matter of necessity. In the conversion of the mono-derivative into a di-derivative, according to the nature of the radicle R′ and also of the reacting molecule, the additive compound will be formed by the attachment of the reacting molecule either to the central carbon-atom contiguous to the radicle R′ or to that which is uninfluenced by a contiguous radicle; or a mixture of the two possible additive compounds may result: and on subsequent decomposition of the additive compound, either a homonucleal or heteronucleal derivative will be formed according to circumstances. The behaviour of β-derivatives of naphthalene is in many respects noteworthy, and I would point to the conversion of betanaphthyl sulphate into Schaefer's betanaphtholsulphonic acid by mere warming (*Ber.*, 1882, 203) as being a most interesting case of isomeric change, especially if considered in connexion with the suggestion previously advanced in explanation of the production of para-di-derivatives of benzene; Schaefer's acid is most probably a $\beta^2\beta^{3'}$-derivative, and its relation to the isomeric sulphate is accordingly represented by the symbols—



Betanaphthyl sulphate.



Schaefer's betanaphtholsulphonic acid.

Even those who are of opinion that para-carbon-atoms in benzene are to be regarded as directly connected will scarcely be willing to admit the existence of any direct connexion between the $\beta^2\beta^{3'}$ carbon-atoms in naphthalene.

The production of haloid derivatives from paraffins may be held to negative the hypothesis advocated in this paper that the formation of additive compounds precedes that of substitution derivatives.' I am of opinion, however, that this is not the case, and that even the paraffins are to a certain extent unsaturated bodies: it is because they are so nearly saturated, I believe, that the lowest terms especially are so slowly acted upon, and it is perhaps noteworthy that nitric and sulphuric acids, which appear to manifest less tendency than do the halogens to form additive compounds, act less readily on paraffins than do chlorine or bromine. But the view here advocated finds its chief support in the behaviour of the mono-haloid-derivatives of paraffins: these, it is well known, are far more readily attacked by halogens than are the paraffins, and thus afford a strong argument in favour of my assumption that negative elements especially tend to attract each other. Without here entering into a full discussion of the subject, I may point out that the laws of addition and substitution generally are for the most part capable of explanation by means of this principle: for example, it is an established rule that in the formation of additive compounds from compounds of the olefine type, the negative radicle of the reacting molecule usually attached itself to the least hydrogenised carbon-atom, propylene, for instance, $CH_3{\cdot}CH{\cdot}CH_2$, forming isopropyl iodide, $CH_3{\cdot}CHI{\cdot}CH_3$, not propyl iodide, $CH_3{\cdot}CH_2{\cdot}CH_2I$: but the less hydrogenised is of necessity the more negative carbon-atom. Again, it is well known that negative radicles tend to accumulate: ethyl chloride, for example, yielding on chlorination as chief product not ethylene but ethylidene chloride, $CH_3{\cdot}CHCl_2$; alcohol yielding on oxidation aldehydrol, $CH_3{\cdot}CH(OH)_2$, not glycol, $CH_2(OH){\cdot}CH_2(OH)$.

I have thought it advisable thus to direct attention to a possible explanation of the laws of substitution, because it appears to me that of late years the subject has not received that amount of consideration which from its importance it deserves—perhaps for want of a guiding principle. As yet but a mere rough survey of this field of inquiry has been effected; true it is that this has enabled us to outline its characteristic features, but the accurate measurement of details which will enable us to draw the finished picture has yet to be accomplished, and will involve patient and prolonged investigation. It is more than probable that I may exaggerate its importance, but it appears to me that the doctrine of "Residual Affinity" of which I have ventured to become the exponent (*Proc. Roy. Soc.*, 1886, **40**, 268), will be of service as a guide in these inquiries.

City and Guilds of London Institute,
Central Institution.

XXIX.—*The Action of Chlorine on Organic Thiocyanates.*
Part I. *Methyl Thiocyanate.*

By J. William James, Ph.D., F.C.S., University College of South Wales, Cardiff.

The action of chlorine on methyl thiocyanate was first investigated by Cahours (*Annalen*, **61**, 96), who found that cyanuric chloride and a heavy oil were formed; some time later, in 1854, Riche studied the reaction more closely (*Annalen*, **92**, 357).

In continuation of my work with ethylene chlorothiocyanate, I was led to examine the action of chlorine on methyl and ethyl thiocyanates, in the hope originally, of obtaining chlorinated thiocyanates as substitution products; but as I have already shown in a short notice (*J. pr. Chem.* **30**, 316) the thiocyanate group is at once attacked by the chlorine, the whole of the cyanogen combining with it to form cyanuric chloride.

The résult of Riche's work with methyl thiocyanate is the formation of cyanuric chloride, and a liquid boiling from 70° to 200°, from which he separated two main products; the one boiling below 86°, stated to be a mixture of sulphur dichloride with carbon tetrachloride, and the other boiling from 140° to 170°, which after shaking with potassium hydroxide, and drying over calcium chloride, boiled at 150° to 160°; this had the composition C_2SCl_6.

100 grams of pure methyl thiocyanate was placed in a flask surrounded by cold water, and a slow stream of dry chlorine passed in, in diffused light. At first very little hydrogen chloride was given off, the chlorine being completely absorbed. The colourless liquid became yellow, and at last deep orange. In about two hours hydrogen chloride is evolved in large quantities, and this continues throughout the reaction, but there is very little rise of temperature. After chlorine had been passed in for five hours, the flask was allowed to stand in a cool place during the night, when a quantity of large, colourless, well-formed monoclinic crystals separated. The supernatant liquid was poured off, and again treated with chlorine to complete saturation, finally in sunlight, and until hydrogen chloride ceased to be evolved, this liquid on standing deposited a fresh quantity of the crystals.

Examination of the Crystals.—These were freed from adhering liquid by pressing them between filter-paper, and further purified by standing over sulphuric acid and lime. A melting point determination gave 146°, and their other properties showed them to be pure cyanuric chloride. Some of the crystals were so large and well formed that it was my intention to have them measured; but this has already been done by Hofmann in his recent work on cyanuric ethers (*Ber.*, **19**, 2063), while these experiments were in progress.

From 100 grams of methyl thiocyanate, I have obtained on an average 65 to 70 grams of pure cyanuric chloride, the calculated quantity being 84 grams, so that this is a most advantageous method for preparing this important substance.

Examination of the Liquid.—The orange-coloured liquid on fractional distillation yielded three fractions: one boiling from 70° to 75°, another distilling from 148° to 150°, and the third, in small quantity, above 200°. From the last fraction I have, in spite of several different experiments, been unable to obtain any definite result. It contains varying quanities of cyanuric chloride, and this cannot be removed by distillation, as the substance is gradually decomposed into a liquid which begins to boil at 70°.

Fraction 70—75°. This is of a deep orange colour, with rod vapour. An analysis showed it to consist of a mixture of thiocarbonyl chloride and carbon tetrachloride, very nearly in the proportion of 2 mols. of the former to one of the latter: $2CSCl_2 + CCl_4$. It is not immediately acted on by water; it may in fact be shaken with it without showing any sign of decomposition, and this proves sulphur dichloride to be absent. It fumes strongly in air, its vapour causes a copious flow of tears. and acts most violently upon the respiratory organs. I obtained as much as 50 grams of this liquid from 100 of methyl thiocyanate, and endeavoured to separate it into thiocarbonyl chloride and carbon tetrachloride by further fractional distillation, but this cannot be done to any extent by observing the thermometer. If, however, the first portion of the distillate be again and again distilled slowly, until about one-fourth has been collected, it will be found to consist almost entirely of thiocarbonyl chloride. One sample prepared in this way weighed 10 grams, and gave the following numbers on analysis :—

I. 0·2856 gram substance, after oxidation with concentrated nitric acid at 200° in a sealed tube, produced 0·541 gram $BaSO_4$ = 26·01 per cent. sulphur.

II. 0·2025 gram substance burnt with lime gave 0·531 gram AgCl = 64·85 per cent. chlorine.

	Calculated for $CSCl_2$.			
C..........	12	10·43		—
S..........	32	27·83	26·01	—
Cl_2	71	61·74	—	64·85
	115	100·00		

The liquid was preserved in a small stoppered cylinder, and after standing a few days, large well-formed rhombic crystals had separated; these were pressed between filter-paper, dried over lime, and analysed. They melted at 115°.

0·2355 gram substance burnt with CuO and $PbCrO_4$ gave 0·004 gram H_2O and 0·0905 gram CO_2.

0·2735 gram substance oxidised with concentrated nitric acid at 200° gave 0·5600 gram $BaSO_4$.

	Calculated for $(CSCl_2)_2$.		Found.	
			I.	II.
C..........	12	10 43	10·48	—
S..........	32	27·83	—	28·12
Cl_2	71	61·74	—	—
	115	100 00		

In the *Annalen*, **167**, 180, B. Rathke describes a polymeric modification of thiocarbonyl chloride, which he obtained by the action of chlorine on carbon bisulphide, and with which these crystals are undoubtedly identical. The properties and reactions have been fully described by Rathke, and I will only add that they *sublime* slowly if kept in a stoppered cylinder, forming extremely well formed, strongly refractive crystals; if heated in a bulb-tube, they vaporise readily, condensing to a beautifully crystalline mass. They are insoluble in water, sparingly soluble in alcohol, and easily dissolved by ether. I have found their melting point to be 114—115°, at which temperature they sublime; Rathke gives 112 5°. He also states in his memoir that "the formation of these crystals seems to depend on the action of light." I have not found this to be the case. Several small cylinders containing thiocarbonyl chloride were exposed to light for several days, but no crystals formed. On opening each of them, crystals immediately made their appearance. A cylinder containing both crystals and liquid was exposed to sunlight, the crystals disappeared, and did not again form, even after an interval of three weeks. On opening and shaking, they immediately reappeared.

Fraction 148—150° (uncorr.). A pale-yellow liquid obtained in much larger quantity than that of low boiling point, which on analysis was found to have the formula $CSCl_4$.

I. 0·3690 gram substance on combustion with CuO and $PbCrO_4$ gave 0·0855 gram CO_2.
II. 0·3185 gram substance gave 0·4375 gram $BaSO_4$ after oxidation by concentrated HNO_3 at 200°.
III. After rectifying again—
0·154 gram substance produced 0·2115 gram $BaSO_4$.
IV. 0·2075 gram on ignition with lime gave 0·6350 gram AgCl.

	Calculated for thiocarbonyl tetrachloride, $CSCl_4$.		Found.			
			I.	II.	III.	V.
C	12	6·45	6·31	—	—	—
S........	32	17·20	—	18·86	18·83	—
Cl_4	142	76·35	—	—	—	75·76
	186	100·00				

The substance probably contains very small quantities of sulphur monochloride, b. p. 138°, and this accounts for the sulphur estimations coming out too high.

This liquid proves to be identical with that which Rathke (*Annalen*, **167**, 180) obtained by the action of chlorine on carbon bisulphide in presence of a small quantity of iodine, and named by him *perchloromethyl mercaptan* from its supposed analogy to methyl mercaptan, with its hydrogen substituted by chlorine, $CCl_3{\cdot}SCl$. This formula is unsupported experimentally, and the substance might, I think, be more conveniently termed *thiocarbonyl tetrachloride*, thus bringing out its analogy to thiocarbonyl chloride, $CSCl_2$,* the constitution of which is also an open question.

From 100 grams of methyl thiocyanate, 83 grams of thiocarbonyl tetrachloride were obtained, after acting on the liquid of low boiling point* with chlorine in order to obtain a maximum yield.

The chief reaction which takes place with methyl thiocyanate and dry chlorine is consequently the following:—

$$3CH_3{\cdot}SCN + 11Cl_2 = Cl_3(CN)_3 + 2CSCl_4 + CSCl_2 + 9HCl.$$

No satisfactory results can be obtained on fractional distillation unless chlorine be passed in, in sunlight, towards the end of the reaction, so as to displace all the hydrogen; as the intermediate products CH_2SCl, CH_2SCl_2, &c., cannot be separated in a sufficiently pure condition.

It seems to me not improbable that the cyanogen-group is attacked first of all, and that the residue (CH_3S) acts just as methy disulphide, $(CH_3)_2S_2$, would. I hope shortly to study the action of chlorine on this substance, and it may possibly prove to be a fruitful method for preparing thiocarbonyl chloride, $CSCl_2$, in quantity.

Action of Chlorine on Thiocarbonyl Chloride, $CSCl_2$. *Formation of Thiocarbonyl Tetrachloride*, $CSCl_4$.

The conversion of thiocarbonyl chloride into thiocarbonyl tetrachloride by assimilation of two atoms of chlorine takes place at ordinary temperatures with the greatest ease.

A slow stream of dry chlorine was passed into a cylinder surrounded by cold water and containing 5 grams of thiocarbonyl chloride. The chlorine is completely absorbed, and in a very short time the liquid changes colour from deep orange to light yellow. On distillation, it was found to pass over almost entirely between 148° and 150° (uncorr.). An estimation of the chlorine gave the following numbers:—

---

* See below "Action of Chlorine on Thiocarbonyl chloride."

0·2775 gram substance ignited with lime, finally produced 0·8520 gram AgCl.

	Calculated for $CSCl_4$.	Found.
Cl	76·35 per cent.	75·95

A few drops of a dark red liquid distilled over first of all; this was not unaltered thiocarbonyl chloride but proved to be mainly sulphur dichloride. It was immediately decomposed by water, becoming coated with a film of sulphur; in odour too, it differed characteristically from thiocarbonyl chloride.

It will be clear from this reaction, that chlorine must be passed into that portion of the liquid of low boiling point obtained in the first rectification, if a maximum yield of thiocarbonyl tetrachloride be required.

Action of Chlorine on Thiocarbonyl Tetrachloride.

The formation of sulphur dichloride in the previous reaction seemed to indicate a decomposition of thiocarbonyl tetrachloride, and this has been proved to be the case.

Chlorine was passed into a flask surrounded by warm water, containing 5 grams of pure thiocarbonyl tetrachloride, for one hour. At the end of this time, there was no perceptible difference in the colour of the liquid, but on distillation about one-third passed over between 60° and 120°, and this consisted mainly of sulphur dichloride and carbon tetrachloride. The presence of the former was easily established by its reaction with water, and after distilling with excess of sodium hydroxide in a current of steam, a liquid was obtained boiling at 78—80°, and having all the properties of carbon tetrachloride. It was evident, then, that the following reaction had taken place:—

$$CSCl_4 + Cl_2 = CCl_4 + SCl_2.$$

The well-known fact that carbon bisulphide is decomposed by dry chlorine almost entirely into sulphur dichloride and carbon tetrachloride, seems in view of these experiments to be the final result of a series of reactions, viz.:—

$$\begin{aligned} CS_2 &+ 2Cl_2 = CSCl_2 + SCl_2, \\ CSCl_2 &+ Cl_2 = CSCl_4, \\ CSCl_4 &+ Cl_2 = CCl_4 + SCl_2. \end{aligned}$$

Returning now to Riche's work on this subject—it is to a large extent inaccurate—his supposed compound, C_2SCl_6, was undoubtedly a mixture of thiocarbonyl tetrachloride, $CSCl_4$, with cyanuric chloride, the latter being lost sight of in consequence of determining the percentage of sulphur by difference and not directly, and assuming carbon, sulphur, and chlorine only to be present. Neither was the liquid of low boiling point analysed; had this been done, it is probable that Kolbe's discovery of thiocarbonyl chloride would have been confirmed a few years after it was made.

Action of Thiocarbonyl Tetrachloride on Alcohol.

Rathke has assumed $CSCl_4$ (perchloromethyl mercaptan) to have the constitution $CCl_3{\cdot}S{\cdot}Cl$, and this assumption is further borne out by its formation from methyl thiocyanate. I have endeavoured to obtain some confirmation of this formula by examining the action of alcohol on this compound. Those atoms of chlorine directly combined with carbon should not be attacked, whereas the group (SCl') would possibly yield $S(OC_2H_5)'$, or, at any rate, be so acted on as to give some insight into its constitution.

The action of alcohol, which I have not yet been able to complete, has produced quite an unexpected result. On mixing thiocarbonyl tetrachloride with twice its volume of absolute alcohol it is dissolved, and in a short time the temperature of the mixture rises very considerably. After digestion on the water-bath, a heavy, yellow oil separates; this cannot be distilled. It is very sparingly soluble in alcohol, insoluble in water, but soluble in ether. Analyses point to the formula CS_3Cl_3; probably $C_2(SCl)_6$.

On fractioning the alcoholic liquid, a substance was isolated which is insoluble in water, and contains neither chlorine nor sulphur. After shaking with a saturated solution of calcium chloride to remove the last traces of alcohol, it boiled at 126°, and analyses indicated that its formula is $C_3H_8O_2$.

XXX.—*The Decomposition of Potassium Chlorate and Perchlorate by Heat.*

By PERCY F. FRANKLAND, Ph.D., B.Sc., A.R.S.M., and JOHN DINGWALL.

SOME interesting points in connection with the decomposition of potassium chlorate by heat were raised by Teed in a paper, the abstract of which was published in the Proceedings of the Society (No. 12, 1885–86). At the suggestion of Professor Thorpe, we have submitted these points to further examination, and have also investigated the behaviour of the perchlorate under the action of heat.

In the first series of experiments brought before the Society by Dr. Teed, he pointed out that when potassium chlorate is heated it first undergoes decomposition according to the equation—

$$10KClO_3 = 6KClO_4 + 4KCl + 3O_2,$$

and not according to the commonly accepted one—

$$2KClO_3 = KClO_4 + KCl + O_2.$$

In these experiments no special method of heating the chlorate was adopted with a view to maintain a constant temperature, and only the loss (calculated as oxygen evolved) and the chloride formed were determined.

In repeating these experiments, we have not only determined the loss and the chloride formed, but also the chlorate remaining unchanged, and we have adopted special precautions to prevent any loss through spurting by plugging the tube in which the decomposition was effected with glass-wool. In some experiments, we have also preserved a constant temperature during the decomposition by placing the tube in the vapour of boiling sulphur instead of heating it with a naked flame.

The potassium chlorate remaining undecomposed after the operation was determined by reducing it with the zinc-copper couple in the manner described by Thorpe (*Chem. Soc. Journ.*, 1882, 547), and then determining the increase in chloride by titration with decinormal silver nitrate, using potassium chromate as indicator.

In these experiments, the following results were obtained (see Table I, p. 276).

In the case of the first two of the experiments recorded above, it will be seen that although very different quantities of oxygen were driven off in the two cases, yet the proportion on the potassium chlorate actually decomposed is almost exactly the same. Moreover, in the quantity of oxygen liberated, and in the chloride and perchlorate formed, the decomposition in each case coincides very closely with the requirements of the equation—

$$8KClO_3 = 5KClO_4 + 3KCl + 2O_2,$$

the coincidence with this equation is far greater than with the more complex equation suggested by Teed—

$$10KClO_3 = 6KClO_4 + 4KCl + 3O_2.$$

In the third experiment, however, in which a larger quantity

I. *Potassium Chlorate heated over Naked Flame.*

Percentage of oxygen evolved on weight of $KClO_3$ taken.	On $KClO_3$ actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	$KClO_4$ formed (per cent.).	Proportion of oxygen evolved to 74·57 parts of KCl formed.
No. 1. 2·66	6·30	22·48	71·22	20·87
No. 2. 5·19	6·27	22·43	71·30	20·84
No. 3. 6·47	7·09	23·68	69·23	22·32
Equation—				
$10KClO_3 = 6KClO_4 + 4KCl + 3O_2$ requires	7·83	24·34	67·83	24·00
$8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ requires	6·53	22·81	70·66	21·33
$2KClO_3 = KClO_4 + KCl + O_2$ requires	13·05	30·42	56·53	32·00

of oxygen was driven off, the results fall intermediate between the $8KClO_3$ and the $10KClO_3$ equations.

It thus appears that the equation representing the decomposition varies as the latter is more or less complete.

As in the above experiments, as well as in those of Teed's, there is no guarantee that the reaction is not complicated through the further decomposition by the naked flame of perchlorate at first formed, it appeared to us desirable to ascertain the nature of the decomposition taking place at a temperature below that at which potassium perchlorate is decomposed.* For this purpose we selected the temperature of boiling sulphur.

The piece of combustion-tubing containing the potassium chlorate was fitted by means of a cork into the tubulure of a retort in which a quantity of sulphur was kept in ebullition, so that the portion of the tube containing the chlorate was completely surrounded by the sulphur-vapour.

In other cases we simply fitted, by means of glass-wool, the tube with chlorate into a boiling tube containing sulphur.

---

* 4·8208 grams of potassium perchlorate, containing 1·35 per cent. of potassium chlorate (as indicated by the zinc-copper couple reaction), were heated for 56 hours in sulphur vapour, and found to lose only 0·0149 gram or 0·3 per cent.

Two of these experiments were carried on simultaneously, the tubes being weighed daily in order to ascertain whether decomposition was still proceeding. The decomposition, which at first was comparatively active, gradually became very sluggish indeed. Thus in the two parallel experiments, in one case 5·3345 grams of chlorate were exposed to the heat of the sulphur-bath for 98 hours, and during the first five hours the loss amounted to 0·1166 gram (2·18 per cent.), whilst in the last five hours the loss amounted to only 8 mgrms., and in the other case 2·5149 grams of chlorate were heated for 79 hours, and lost during the first seven hours 0·0686 gram (2·72 per cent.), and during the last five hours only 0·2 mgrm.

The residues were treated as before described in the case of the naked flame experiments, and the following results were obtained*:—

II. *Potassium Chlorate heated in Sulphur-vapour.*

Percentage of oxygen evolved on weight of $KClO_3$ taken.	On $KClO_3$ actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	$KClO_4$ formed (per cent.).	Proportion of oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·89	8·14	25·44	66·42	23·88
No. 2. 6·78	8·76	26·03	65·21	25·10
No. 3. ($KClO_3$ mixed with powdered glass) 14·30	15·34	33·55	51·11	34·10

In all three cases, the decomposition of the chlorate was incomplete, for in each case the residue contained unchanged chlorate as well as the chloride and perchlorate formed by the decomposition of the original salt.

It will be seen that in experiments Nos. 1 and 2 the decomposition had gone further than is indicated by the $8KClO_3$ equation, No. 1 agreeing fairly well with the $10KClO_3$ equation, whilst in No. 2 the decomposition had gone even beyond that.

It is especially noteworthy that when the chlorate was mixed with half its weight of powdered glass the decomposition of the chlorate was almost complete, and that it took place more nearly according to the old equation, $2KClO_3 = KClO_4 = KCl + O_2$.

It would appear, therefore, that when potassium chlorate is partially decomposed by heat, the decomposition takes place according to equations of the type $8KClO_3 = 2O_2 + 5KClO_4 + 3KCl$, and that the more complete the decomposition is the more does it approximate to that indicated by the equation

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Decomposition of Potassium Perchlorate.

In Dr. Teed's second communication on potassium chlorate (Proc., 1885–86, p. 141), he incidentally mentions that, in the decomposition of potassium perchlorate by heat, potassium chlorate is at first formed. This point appeared to us of particular interest as being opposed to Berthelot's "principe du travail maximum" (*Essai de Mécanique Chimique, fondé sur la thermochimie*, 2, 421, 1879), which asserts that every chemical change taking place without the intervention of any foreign energy tends to the production of that body or system of bodies which generates the greatest amount of heat. Now, as is well known, in the production of potassium chlorate a large amount of heat is absorbed which is subsequently liberated in its decomposition.

As the only evidence adduced by Teed in support of this production of potassium chlorate, was the liberation of a larger quantity of oxygen, in proportion to the potassium chloride formed, than is required by the equation

$$KClO_4 = KCl + 2O_2,$$

it appeared to us desirable to place this interesting formation of potassium chlorate on a surer foundation.

For this purpose the following experiments were undertaken:—

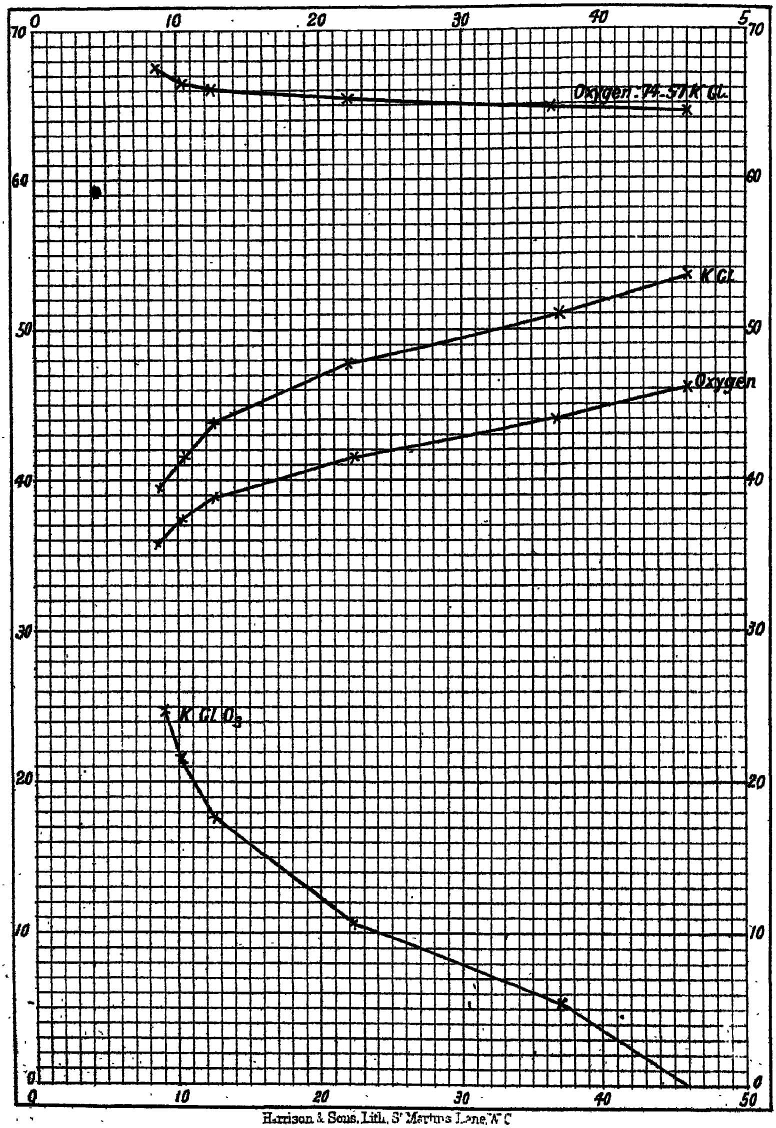
The potassium perchlorate which we first employed, although the purest commercially procurable, was found by means of the zinc-copper couple reaction to contain 1·35 per cent. of potassium chlorate.

Portions of this potassium perchlorate were heated over a naked flame in a piece of combustion-tube sealed at one end and loosely plugged with glass-wool at the other. The heating was continued so as to liberate a different proportion of oxygen in each experiment. In each case, the residue was dissolved in water, the chloride determined by means of decinormal silver nitrate in one portion, and in another the increase in chloride obtained by reduction with zinc-copper couple was ascertained and calculated as chlorate. In this manner, the following results were obtained (see table, p. 279).

Excluding experiment No. 2, it will be seen that the results form a continuous series, the proportion of chlorate formed diminishing as the oxygen liberated increases, whilst the chloride formed increases with the proportion of oxygen evolved. The relationship between

Journ. Chem. Soc. March 1887.

DECOMPOSITION OF POTASSIUM PERCHLORATE BY HEAT.



Harrison & Sons, Lith, St Martins Lane, W.C.

Decomposition of Potassium Perchlorate.

Percentage of oxygen evolved on weight of $KClO_4$ taken.	Results on potassium perchlorate decomposed.			
	Oxygen evolved (per cent.).	KCl formed (per cent.).	$KClO_3$ formed (per cent.).	Oxygen to 74·57 parts of KCl formed.
No. 1. 8·77	35·69	39·46	24·85	67·44
No. 2. 9·76	37·37	40·96	21·67	68·04
No. 3. 10·17	37·06	41·48	21·46	66·61
No. 4. 12·53	38·84	43·67	17·49	66·32
No. 5. 22·12	41·76	47·61	10·63	65·41
No. 6. 36·81	44·01	50·72	5·27	64·71
The equation— $KClO_4 = KCl + 2O_2$ requires	46·19	53·81	—	64·00
No. 7. Potassium perchlorate and MnO_2 heated in sulphur vapour until of constant weight 46·98	46·98	52·65	—	66·54

the three products of decomposition is rendered most apparent by means of the accompanying diagram, in which the abscissæ represent the percentages of oxygen evolved on the weight of perchlorate taken, whilst the ordinates serve to indicate respectively the proportions of potassium chlorate, chloride, and oxygen formed on the weight of perchlorate actually decomposed, as well as the proportion of oxygen liberated to 74·57 parts of potassium chloride formed. In experiment No. 7, a mixture of potassium perchlorate and peroxide of manganese was heated in sulphur vapour until no further loss in weight took place. In this case, the decomposition of the perchlorate to chloride and oxygen was complete, the slight divergence from the requirements of the equation being due to the evolution of a little chlorine, the odour of which was distinctly perceptible at the commencement of the decomposition. On this account, the oxygen evolved (calculated directly from the loss in weight) is above the theoretical, the chloride below, and consequently the proportion of oxygen to chloride markedly above that indicated by the equation.

As in the above experiments the evidence that potassium chlorate is formed was still somewhat indirect, being dependent on the differential result obtained by the action of the zinc-copper couple, we proceeded to prove its formation more directly by partially decomposing a considerable quantity of the same perchlorate and then obtaining the chlorate from the residue by fractional crystallisation.

For this purpose about 47 grams of potassium perchlorate (containing 1·35 per cent. of potassium chlorate) were heated in four separate portions so that each suffered a loss of about 10 per cent. The residues were then united, dissolved in water, and submitted to fractional crystallisation; eventually the following eight fractions were obtained, each of which was qualitatively tested for chloride with silver nitrate, and for chlorate with hydrochloric acid:—

Fraction No. 1.—No perceptible chlorate reaction, but very slight opalescence with silver nitrate.
Fraction No. 2.—No perceptible chlorate reaction, but distinct reaction with silver nitrate.
Fraction No. 3.—Very decided chlorate reaction.
Fraction No. 4.—Ditto.
Fraction No. 5.—Ditto, but not quite so strong.
Fraction No. 6.—No chlorate reaction, but copious precipitate with silver nitrate.
Fraction No. 7.—Ditto.
Fraction No. 8.—Ditto.

Fractions Nos. 3, 4, and 5 were then submitted to analysis, with the following result:—

	No. 3.	No. 4.	No. 5.
KCl	2·60	48·29	82·62
$KClO_3$	41·68	42·91	14·58
$KClO_4$	55·72	8·80	2·80
	100·00	100·00	100·00

These results leave absolutely no doubt as to the presence of potassium chlorate in the residue from the partial decomposition of the perchlorate, and, moreover, assuming that the whole of the chlorate originally present in the perchlorate as an impurity had remained undecomposed during the heating, this would account for only 0·6416 gram $KClO_3$ in the residue, whilst the total quantity of $KClO_3$ found in the above three fractions submitted to analysis amounted to 1·4771 gram, or to 3·1 per cent. of the potassium perchlorate operated on.

In order, however, to render the proof still more complete, we endeavoured to obtain some perchlorate practically free from chlorate altogether, and for this purpose we twice recrystallised the sample of perchlorate used in the former experiments. In order to test the freedom of this perchlorate, thus obtained, from chlorate, we evaporated weighed quantities of it with dilute hydrochloric acid on the water-bath to dryness, then dissolved in water, and again took to dryness, and repeated this operation once more in order to ensure the expulsion of all the excess of hydrochloric acid. Since the perchlorate was proved to be absolutely free from chloride in the first instance, any chloride now present must have been derived from the decomposition of chlorate by the hydrochloric acid added. Two gravimetric determinations of the chloride thus formed by evaporation with hydrochloric acid, showed the presence of potassium chlorate in the purified perchlorate to the extent of—

	I.	II.
$KClO_3$ per cent.	0·29	0·21

This perchlorate was thus practically free from chlorate.

N.B.—The zinc-copper couple method was not employed for determining this trace of chlorate for reasons which are apparent from the note appended to this paper.

With this purified perchlorate, a series of decomposition experiments was made similar to that above described, with the exception that the chlorate was determined by evaporation with hydrochloric acid, instead of by means of the zinc-copper couple reaction.

The following results were obtained:—

Decomposition of Potassium Perchlorate (2nd Series).

Percentage of oxygen evolved on weight of $KClO_4$ taken.	On $KClO_4$ decomposed.			
	Oxygen evolved (per cent.).	KCl formed (per cent.).	$KClO_3$ formed (per cent.).	Oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·34	36·54	38·70	24·76	70·41
No. 2. 7·80	36·63	38·79	24·58	70·42
No. 3. 24·05	43·60	49·21	7·19	66·06
The equation— $7KClO_4 = 2KClO_3 + 5KCl + 11O_2$ requires	36·29	38·44	25·27	70·40

The results of experiments I and II agree very closely with the requirements of the equation $7KClO_4 = 2KClO_3 + 5KCl + 11O_2$, whilst in No. III the decomposition had been carried very much further. These results substantiate those previously made with the less pure samples of perchlorate, and thus the formation of potassium chlorate is demonstrated beyond doubt.

Note on the Action of the Zinc-copper Couple on Potassium Perchlorate.

In attempting to estimate the small proportion of chlorate in the purified potassium perchlorate, the results of duplicate determinations were found to vary considerably. This could only be accounted for on the supposition that by the prolonged action of the zinc-copper couple on the perchlorate a small quantity of the latter had become decomposed. That this actually takes place was clearly proved by the following experiments:—

I. A solution of 5·8057 grams of the purified perchlorate was boiled for one hour with the couple, then allowed to stand over night, the liquid being again heated up on the following morning, and the couple then filtered off. By gravimetric determination, a quantity of chloride was found corresponding to 0·77 per cent. of $KClO_3$.

II. A solution of 3·2251 grams of the same perchlorate was boiled for two hours with the couple and then immediately filtered. Gravimetric analysis showed the presence of chloride corresponding to 0·65 per cent. of $KClO_3$.

III. A solution of 1·0422 grams of the same perchlorate was boiled with the couple for two hours, then allowed to stand over night, then heated up again on the following morning and filtered. The chloride found corresponded to 1·48 per cent. of $KClO_3$.

IV. A solution of 5·0447 grams of the same perchlorate was treated side by side with No. III in precisely the same way. The chloride found corresponded to 1·28 per cent. $KClO_3$.

V.' A solution of 5 grams of the same perchlorate was boiled with the couple for about three hours on December 11th, 1886. The liquid was allowed to stand over till December 13th, when it was boiled for five hours with the same couple, the latter was then filtered off and a new couple added, with which the solution was again boiled. On December 14th it was again boiled all day with the same couple. On December 15th it was boiled with a new couple. On December 16th the boiling with the same couple was continued. On December 17th the solution was boiled with a new couple. On December 18th the boiling was continued with the same couple (the fourth), the liquid was then filtered and the chloride gravimetrically determined, the latter corresponded to 2·49 per cent. of $KClO_3$.

It thus appears that by the continued action of the couple, especially when the latter is renewed, the perchlorate undergoes partial and very slow reduction to chloride.

That this action has not materially affected the results recorded in this paper is clear from the fact that the second series of experiments made with the perchlorate substantiate the first, although in the second series the zinc-copper couple method was not resorted to for the determination of the chlorate, the proportion of the latter being ascertained by decomposition with hydrochloric acid, which has no action on potassium perchlorate.

XXXI.—*Potassium Chlorate and Perchlorate.*

By Frank L. Teed, D Sc.

The results published in the preceding paper by Dr. Percy Frankland and Mr. Dingwall in the main corroborate those obtained by me. Short abstracts of my two papers on this subject appear in the "Proceedings" Nos. 12 and 16 of 1885–86.

Frankland and Dingwall give the equation $8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ as representing the course of the reaction when potassium chlorate is heated over a naked flame, and point out that their results tally better with this equation than with the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$, which I originally suggested. They omit, however, all reference to the equation proposed in my second paper ("Proceedings" No. 16), $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$, whereas if my two equations are added together, and the resulting equation reduced to its lowest terms (dividing by four), it gives the equation $8KClO_3 + 5KClO_4 + 3KCl + 2O_2$, proposed by Frankland and Dingwall, which is merely one of an indefinite number of equations within the limits of my two.

I may point out that when the decomposition is fairly brisk, the results agree more nearly with the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$, and it is noteworthy that in this equation the amount of oxygen that is evolved in the free state is equal to the amount that goes to form perchlorate.

There seems to be an idea that in order to construct an equation representing the decomposition, data are required other than the determination of the evolved oxygen and of the potassium chloride produced, and that it is necessary to determine directly the perchlorate formed, or at all events the undecomposed chlorate. This is erroneous, for it is obvious that for every 74·5 parts of potassium chloride formed, there must have been 122·5 parts of potassium chlorate decomposed, and of the 48 parts of oxygen thereby eliminated, what is not evolved in the free state *must* have gone to form perchlorate. Any direct determinations of the potassium chlorate and perchlorate are therefore unnecessary, but would form a most rigorous test of the accuracy of any process for determining chlorates in presence of perchlorates. From this it will be seen that the data I employed are as sufficient for the determination of the perchlorate formed and of the remaining undecomposed chlorate as the determination of the oxygen lost when copper oxide is heated in hydrogen, and of the water formed, are for ascertaining the composition of water. To give the results in my second paper,* I found that when the chlorate was very gently heated, the products obtained agreed more nearly with the 22$KClO_3$ equation, which demands 20 of oxygen to 74·5 of potassium chloride. In order to give some idea of what I mean by gentle heating, I may state that it took an hour and a quarter to evolve the 1·27 per cent. of oxygen in Experiment No. 2.

No.	$KClO_3$ taken, in grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1......	4·3782	3·60	11·58	23 16
2......	6·865	1·27	4·73	20·00
3......	9·291	1·61	6·00	19·99
4......	4·759	1·60	6·14	19·41
5......	4·4905	1 47	4·84	22·63
6......	6·050	0·80	2·18	27·34

In Experiment No. 6 the chlorate was heated strongly for a very short time, so as to demonstrate that the results varied according to the treatment rather than according to the amount of oxygen evolved.

As Frankland and Dingwall thought that when the chlorate was heated over the naked flame, there was a considerable risk of decomposing the perchlorate formed, they made experiments where the chlorate was heated in sulphur vapour; but under these circumstances they obtained less perchlorate than when the naked flame was employed. They also give the result of an experiment in which a mixture of the chlorate with powdered glass was heated in sulphur vapour; this yielded much less perchlorate than in any other of their experiments. It is difficult to reconcile this with the stability of perchlorate under these particular conditions. I have shown that powdered glass does not affect the decomposition of the chlorate. In one experiment, I took 3 660 grams of potassium chlorate, mixed with 1·697 grams of powdered glass, and heated the mixture until 4·29 per cent. oxygen was lost, and 12·49 per cent. of potassium chloride formed. By calculation, the resulting products were—

---

* The paper was not published in full, and the data do not appear in the Proceedings.

$KClO_3$.	$KClO_4$.	KCl.	O.	
50·67	32 55	12·49	4·29	= 100

with a ratio of KCl : O = 74·5 : 25·59.

I do not in the least dispute Frankland and Dingwall's results as to the stability of the perchlorate heated *per se* in sulphur vapour, but in the light of my experiment with powdered glass I think their result tends to show that a solution of perchlorate in chlorate and chloride is decomposed at that temperature.

In leaving the subject of the chlorate, I may repeat what I said in my former paper, that no equation can be given which represents the decomposition of potassium chlorate when heated, and only proposed the two I have submitted as marking the usual limits of the reaction.

The results of the decomposition of the perchlorate by heat given in my second paper were—

No.	Amount of $KClO_4$ taken, in grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1......	2·4355	3·10	2·97	77·76
2......	3·8825	4·47	4·41	75·59
3......	1·850	7·30	7·82	69·55
4......	1·217	35·21	40·33	65 04

Frankland and Dingwall have lost the first high ratios of oxygen to potassium chloride by driving off too much oxygen, so that their results are incomplete. It is obvious that potassium perchlorate, if it loses more oxygen than is expressed by the equation $KClO_4 = KCl + 2O_2$, must be forming a lower oxide of potassium chloride (if I may be allowed to use such an expression), and the only oxide possible under the circumstances is the chlorate. This, as I stated in the discussion on the reading of my second paper (January 21st, 1886), was further corroborated by adding a drop of sulphuric acid to the product, neither perchlorate nor a mixture of perchlorate with chloride giving the peculiar yellow produced by the chlorate. No other explanation than the formation of chlorate being possible, and its presence being further demonstrated by this direct test, I consider that I fully proved its formation, Messrs. Frankland and Dingwall's experiments merely confirming the results I had already obtained.

In my second paper I also showed that no chlorate was formed on heating perchlorate with manganese binoxide. The following are the results:—

$KClO_4$ taken, grams.	MnO_2 taken, grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1·2305	1·409	14·87	17·22	64·33
1·841	2·5985	5·35	6·24	63·87

In carrying out these experiments, I estimated the oxygen by loss of weight and the potassium chloride by standard silver nitrate solution with potassium chromate as indicator, and used a small stoppered retort as the decomposing vessel, keeping back all fumes by a cotton-wool plug. I consider that it is far better to employ a retort than a tube, because with the former in experiments of this character, it is very easy to displace rapidly all the oxygen by air before weighing, whereas in a plugged tube a very appreciable time must be allowed to elapse before the oxygen can diffuse out.*

---

* As the capacity of the tubes employed by Messrs. Frankland and Dingwall in their experiments was only about 10 c.c., the error introduced from imperfect removal of the oxygen by diffusion would be inappreciable; even supposing there were no diffusion whatever, the increase in weight would not amount to more than 0·0006 gram, when it is remembered that air must enter through the plug as the tube cools.—[EDITOR.]

XXXII.—*On the Formation of Ethylic Cyanacetoacetate.*

By J. WILLIAM JAMES, Ph.D., F.C.S., University College of South Wales, Cardiff.

FIFTY grams (1 mol.) of pure ethylic monochloracetoacetate boiling at 195—197° were poured into a suitable flask containing 40 grams (2 mols.) of finely ground potassium cyanide and about 700 c.c. 99·5 per cent. alcohol. As the action takes place slowly in the cold, it is advisable to allow the flask to stand a few hours with frequent shaking before completing the reaction by digesting for an hour or so on a water-bath. The potassium cyanide is replaced by a dense precipitate of potassium chloride, which contains but traces of the former.

The alcoholic solution, now deep-brown in colour, and smelling very strongly of hydrocyanic acid, was filtered from the potassium chloride, and the alcohol distilled off on a water-bath. The distillate contained large quantities of hydrocyanic acid, much larger than could be expected had the chlorine simply been displaced by cyanogen, and its occurrence due to decomposition or some secondary reaction.

The residue in the retort deposited indistinct crystals on cooling; these were thoroughly freed from the mother-liquor by pressing them between filter-paper, washed with cold alcohol, which removed a good deal of the brown colouring matter, and twice recrystallised from strong alcohol. The substance was now free from chlorine and consisted of microscopic needles aggregated in nodular groups.

A complete analysis of this compound, which was not perfectly white, yielded the results in I.

After recrystallising six times, lastly from 90° per cent. alcohol, very long, slender needles were obtained, consisting of pure *potassiocyanacetoacetate of ethyl* (II).

I. 0·172 gram substance burnt with CuO, $PbCrO_4$, and copper spiral gave 0·067 gram H_2O and 0·2791 gram CO_2.

0·177 gram substance, after ignition and moistening with H_2SO_4, produced 0·0855 gram K_2SO_4.

0·3055 gram substance burnt with CuO and copper spiral gave 23·3 c.c. moist nitrogen at 24·5° and 742 mm.

II. 0·1875 gram substance on combustion gave 0·0695 gram H_2O and 0·2991 gram CO_2.

0·135 gram substance produced 0·0615 gram K_2SO_4.

	Calculated for $CH_2(CN)\cdot CO\cdot CHK\cdot COOEt$.		Found.	
			I.	II.
C_7	84	43·52	44·25	43 50
H_8	8	4·14	4·32	4·11
N	14	7·25	8·34	—
O_3	48	24·89	—	—
K	39	20·20	21·65	20·41
	193	100·00		

The formation of this salt was quite an unexpected result; it probably takes place in two stages: first, the production of ethylic potassio-monochloracetoacetate, with evolution of hydrocyanic acid, ethylic monochloracetoacetate having strongly acid properties; and then secondly, the ethylic potassio-monochloracetoacetate is acted on by another molecule of potassium cyanide, according to the following equations:—

$$CH_2Cl\cdot CO\cdot CH_2\cdot COOEt + KCN = CH_2Cl\cdot CO\cdot CHK\cdot COOEt + HCN$$

$$CH_2Cl\cdot CO\cdot CHK\cdot COOEt + KCN = CH_2(CN)\cdot CO\cdot CHK\cdot COOEt + KCl.$$

Ethylic potassiocyanacetoacetate crystallises from 90 per cent. alcohol in long, colourless needles, which have a bitter taste. It is insoluble in ether and benzene; neither of these liquids remove the brown colouring matter from which it is very difficult to purify the salt.

The yield is a very poor one; from 50 grams of ethylic monochloracetoacetate, one or two grams of pure salt can be obtained; in fact, it seems to decompose by simply dissolving in alcohol, in which it is moderately soluble, for the alcoholic solution always becomes brown, even if the salt be nearly colourless to begin with.

Action of Dilute Acids on Ethylic Potassiocyanacetoacetate.

Five grams of pure ethylic potassiocyanacetoacetate dissolved in cold water were acidified with dilute hydrochloric acid, and the colourless oil which separated was removed by shaking out with ether. After drying by calcium chloride, the ethereal solution was allowed to remain over sulphuric acid and lime in a vacuum until all ether and traces of hydrochloric acid were absorbed. A slightly yellow-coloured oil now remained, which is decomposed by distillation.

An analysis showed it to be pure *ethylic cyanacetoacetate.*

0·1685 gram substance after combustion with CuO and copper gave 0·0915 gram H_2O and 0·3335 gram CO_2.

	Calculated for $CH_2(CN)\cdot CO\cdot CH_2\cdot COOEt$.	Found.
C................	54·19	53·97
H...............	5·80	6·03

Ethylic cyanacetoacetate is a colourless liquid which cannot be distilled under the ordinary pressure. During the winter months, it solidified to a mass of fine, silky needles melting at 26·5°. Once melted, it will not resolidify, unless cooled to near the freezing point. A drop shaken with water and added to ferric chloride gives a red coloration.

It is insoluble in water, but dissolves in alcohol and ether. The products of its decomposition with alkalis have not been thoroughly examined, but acetic acid is undoubtedly produced.

Action of Potassium Cyanide on Ethylic Dichloracetoacetate.

Fifty grams of pure ethylic dichloracetoacetate were poured into a litre flask containing 50 grams of potassium cyanide and about 600 c.c. 99·5 per cent alcohol. The reaction, just as with the monochloracetoacetate, takes place slowly at the ordinary temperature; after standing some time with frequent shaking, the mixture was digested on the water-bath. Little or no potassium chloride separated, but on cooling a large quantity of a salt crystallised out in shining laminæ, containing chlorine, but no nitrogen, and which gave no oily drops on acidifying with dilute hydrochloric acid.

After twice recrystallising from strong alcohol, the substance gave the following analytical results:—

I. 0·2280 gram substance burnt with CuO and $PbCrO_4$ gave 0·0170 gram H_2O and 0·1180 gram CO_2.

II. 0·193 gram substance ignited with lime finally produced 0·3345 gram AgCl.

III. 0·278 gram substance, after ignition and treating with sulphuric acid, produced 0·1475 gram K_2SO_4.

	Calculated for $CHCl_2\cdot COOK$.		Found.		
			I.	II.	III.
C_2	24	14·37	14·11	—	—
H........	1	0·60	0·82	—	—
Cl_2.......	71	42·51	—	42·82	—
O_2........	32	19·17	—	—	—
K........	39	23·35	—	—	23·78
	167	100·00			

The salt was therefore *potassium dichloracetate;* it agreed in properties with Wallach's description of this salt (*Ber.*, 1873, 114).

It was certainly to be expected that potassium cyanide would behave towards ethylic dichloracetoacetate in a manner analogous to that which it did with the monochlorinated derivative—if not both atoms of chlorine, the displacement of at least one was expected—but no such action appears to have taken place, even to a small extent; this is borne out by the fact that the yield of potassium dichloracetate is almost the theoretical.

The reaction which occurs may be represented by the following equation:—

$$CHCl_2\cdot CO\cdot CH_2\cdot COOEt + KCN + H_2O = CHCl_2\cdot COOK + HCN + CH_3\cdot COOEt.$$

I am not aware that any such case as this has been previously described; that is, one in which two haloïd derivatives of ethylic acetoacetate react with the same substance in such a widely different way. It would be interesting to ascertain whether other substances, sodium ethylate, for example, act similarly.

It is necessary to state that the ethylic monochloracetoacetate was prepared by passing chlorine into well-cooled ethylic acetoacetate until 100 grams had gained 30 grams in weight, the pure substance being easily isolated by fractional distillation, after removing the dissolved hydrogen chloride by washing with water and desiccating with calcium chloride.

The ethylic dichloracetoacetate I employed was made by saturating ethylic acetoacetate with chlorine, the flask being kept cool; after removing the hydrogen chloride as above, subsequent rectification yielded the pure substance, boiling at 205—210°.

Geuther's Laboratory,
University of Jena, September, 1886.

XXXIII.—*The Influence of Temperature on the Heat of Dissolution of Salts.*

By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College.

In March last year, I brought before this Society the results of an investigation on the influence of temperature on the heat of chemical combination (Trans., 1886, 260), which tended to show that the heat evolved or absorbed when a salt is dissolved in water does not vary continuously with an alteration in temperature, but that irregularities occur at intervals only a few degrees apart, indicative of alterations in the complexity of the molecular groupings present, and indicating at the same time variations of a less marked character in the heat of combination of the solid salt with its water of crystallisation. These results were subsequently criticised and disputed by Professor Tilden (Proc., No. 24, 198). The general fairness of this criticism I willingly admit, although I cannot agree with it in all its details. A worker is no doubt apt to be misled by having had for a long time too close and, perhaps, a one-sided view of his own work, but something must also be subtracted from the critic's opinion, from the fact that he has not followed the work in the whole of its progress, especially so when he himself has performed work of a similar nature, but under totally different conditions, and with different and comparatively imperfect instruments. So far, however, as his general conclusions went, I must admit that I believe Professor Tilden was right, and my thanks are therefore due to him for exposing my error. The peculiarities which I noticed in the lines representing the heat of dissolution, consisted of indentations occurring at various points, converting these lines into a series of curves: as to the existence of such indentations I now consider that I was quite wrong; they do not exist: but that changes more or less sudden do occur in these lines, and in the nature of the molecular aggregates of a salt in solution, the present work will, I trust, place beyond a doubt. I can scarcely attribute the errors into which I was led in the first instance to carelessness or insufficient work, the multiplicity of the experiments and of the different instruments used in them might have been reasonably taken as a safeguard against error, and from want of other adequate causes I can only attribute the error which did occur to peculiarities in these instruments, and in thermometers in general, although there are various reasons which render such an explanation unsatisfactory.

The objections which Professor Tilden raised against my work were three in number. First, that I trusted too much to mean results, independent of the value of the individual experiments constituting the mean. This, I hope, I have obviated in the present instance: all results which appeared exceptional were repeated, and such alterations in the lines as exist depend, as will be found, on series of experiments extending over many degrees, and not on experiments at one particular temperature only; moreover, no alterations are insisted on unless they are clearly shown by at least two whole series of experiments performed with different instruments.

The second objection raised was the difficulty of acurately ascertaining the correction for cooling (or heating) during the experiment. Here, I think, Professor Tilden has been misled by his own experience derived from experiments in which the correction for cooling attained very much larger proportions than in the present work. After the salt has been introduced and dissolved the thermometer was read at intervals of two minutes in order to determine the rate of cooling, and from it the corrected final temperature. The average cooling during these two-minute intervals amounted to less than 0 01°, and, as the rate given by the first two observations did not differ generally by more than 0·001°, the error in applying this correction cannot be very large. If the variation was greater than 0·001°, a larger number of observations were made. Owing to the rate of cooling being so small, it remains quite constant throughout the whole experiment.

The last objection was a more subtle one. The rate of cooling may be determined with accuracy, Professor Tilden suggests, but while the salt is dissolving there is a period when the temperature is rising (or falling), and during this period the rate of cooling is uncertain; this period, moreover, will vary in length as the temperature is higher or lower, and any errors in the correction applied for it may attain much greater dimensions at lower than at higher temperatures. It may be pointed out in the first place that such errors would not cause any *sudden*, but only a *gradual* alteration in the results; Professor Tilden, however, greatly overestimates the difficulties of the case. It is true that the salts do take longer to dissolve at low temperatures than at high ones, but in the present instances this difference is quite inappreciable. The time thus occupied was ascertained in a few cases at widely different temperatures; the moment the thermometer was read, the moment when the salt first touched the water, and the moment when the thermometer attained its maximum (or within 0·1° of its final position), being noted with the help of an assistant. The results were as follows:—

Anhydrous Strontium Chloride.

	At 24°.		At 23°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	12		14	
Maximum attained......	26	14	27	13

Mean interval 13·5 sec.

	At 5°.		At 4°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	15		15	
Maximum attained......	26	11	31	16

Mean interval 13·5 sec.

Anhydrous Sodium Acetate.

	At 24°.		At 23°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	16	24	16	26
Maximum attained......	40		42	

Mean interval 25 sec.

	At 5°.		At 4°.	
	Sec.	Interval.	Sec.	Interval.
Temperature read	0		0	
Salt added	17	23	15	25
Maximum attained......	40		40	

Mean interval 24·5 sec.

Thus, although there is a difference of 20° between the two pairs of experiments in each case, the interval elapsing between the moment when the salt first touched the water and that when the thermometer reached its maximum is the same within one second. These two salts were selected owing to their being extreme cases in opposite directions; strontium chloride may be added to the water very quickly, whereas sodium acetate must be added more slowly, and floats some time on the surface of the water before sinking. The uncertain interval, therefore, during which the thermometer is rising may be taken to be on an average the mean of these two, namely, 19 seconds, while the average rate of cooling after the maximum is attained is, as mentioned above, 0·045° per minute. During the uncertain interval, the rate of cooling is somewhere between that of the initial temperature (the rate there is *nil*) and that of the final temperature; I assume that it is exactly intermediate between them; hence on an average the amount of cooling during this uncertain interval would be $\left(\frac{19}{60} \text{ of } \frac{0{\cdot}0045}{2} = \text{not much over}\right)$ 0·0005°, a quantity almost negligible: where, therefore, the total correction is so small, the error which it may contain is surely not worth consideration.

Apparatus.

In the present series of experiments, the apparatus employed was far more perfect than in the previous work. The contents of the calorimeter were stirred by means of a platinum rod with three blades arranged like a screw at the lower end; this was rotated by means of an electromotor. The results with this stirrer were found to be very satisfactory when the motor was worked by a battery of some constancy; if, however, the battery is not constant the rate of cooling will be irregular.

The thermometers were suspended immediately above the rotating arms, and were tapped on the upper end continuously by means of clockwork apparatus. They were read with a cathetometer, and hence, except to add the salt, the operator never approached the calorimeter. The salts were weighed out into test-tubes on feet, as in former experiments, and were left till they had attained the temperature of the air of the laboratory, an hour and a half being found requisite for this, and were protected from draughts meanwhile by being surrounded with a water-jacket, similar to that of the calorimeter itself, but covered at the top; in this vessel, a delicate thermometer was suspended. The air was kept constant within 0·1° of the initial temperature of the experiments. A very simple arrangement was adopted after a time for preventing salts from splashing when shaken out into the calorimeter, consisting of a small piece of platinum gauze hanging on the edge of the calorimeter, and immersed about $\frac{1}{8}$-inch below the surface of the water.

Thermometers.

The thermometers employed in this work were two in number (Nos. 65108 and 65561, by Casella), both different from any used in the previous work. They were both made out of the same cane, and their bulbs contained 39 and 46 grams of mercury respectively. The value of 1 millimetre of the mercurial column was 0·0116° and 0·0097°, an estimation figure of 0·05 mm., corresponding, therefore, to about 0·0005° C.

The production of these instruments was the result of some years labour and repeated failures. The delicacy of a thermometer depends, of course, on the fineness of the bore of the tube and the size of the bulb; but many unexpected difficulties are met with when we push both these conditions to their extreme limits. Tubes of the requisite strength and of very fine bore can be obtained by chance only; from the glassblower's point of view, indeed, they are failures, and he tries to avoid producing them; moreover, such as are sometimes produced are generally too flat in the bore to be suitable for a really fine instrument. The bore should be flat, but at the same time well rounded at the edges, for if the edges be wedge-shaped the mercury will often not entirely fill the tube, and the instrument will be untrustworthy and useless.

The impossibility of obtaining a suitable tube forced me to reduce the delicacy of my present instruments to less than the delicacy which

I had obtained in some previous ones (0·0003°). The bulb of the instrument presents fewer difficulties. though long practice only can give the experience which is necessary to tell whether the mercury in it has been efficiently boiled. The pressure of the column of mercury in the tube of these delicate instruments produces an expansion of the bulb, which attains very considerable apparent dimension. Thus with one of my thermometers there would be as much as 20 or 30 mm. difference in the reading of the same temperature, according as the instrument was held in a vertical or horizontal position. The variations of pressure on the bulb produced by the alteration in the height of the column are not considered, however, to affect the accuracy of the measurements, provided the thermometer be always held in the same position, since the expansion of the bulb is directly proportional to the pressure (Egen, *Pogg. Ann.*, **11**, 283; Mills, *Proc. Roy. Soc. Edin.*, **29**, 285); but this, I find, is not entirely true: the expansion *is* directly proportional to the pressure, but it is apt to take place in an irregular manner, resembling the sudden alterations in shape which may often be noticed when increasing the pressure on a thin tinplate vessel. Serious errors may thus arise, and the only way in which they can be obviated is by increasing the strength, and thus diminishing the expansibility of the bulbs. This I effect by having the bulbs made out of carefully selected glass cylinders, and not blown before the lamp; much greater uniformity in substance and regularity of action is thus obtained. A further large increase of rigidity is obtained by having a double bulb instead of a single one. The walls of the tubing out of which the bulb is made may be of considerable thickness without diminishing the sensitiveness of the instrument to any appreciable extent, provided always the thermometer is to be employed in taking the temperatures of liquids, and that the agitation of the liquid be perfect. I use tubing as much as 0·7 mm. thick in the walls for bulbs containing 30—50 grams of mercury, and find that the temperature of the liquid is attained in about five seconds. The coefficient of expansion of the bulb of a thermometer of the delicacy of those here discussed should not be much more than 0·00000003 per mm. of mercury pressure; with a coefficient of 0·000000045 I have noticed considerable irregularities in the expansion.

One point which is of vital importance in the construction of a delicate thermometer is that the interior of the tube should be protected from contact with the air. The more delicate instruments which I employed formerly had the serious defect of giving a different reading according as the column had risen or fallen to the position of rest, and after much trouble this defect was traced to the fact that the instruments had been opened after they had been made up, a temporary bulb having been attached at first for the purposes of calibration. It was found that such an operation entirely ruined the tube, and that it was only by observing the most minute precautions, and by never opening the tube till the moment the bulb was ready to be attached that a perfect instrument could be produced. By exposure to the air glass absorbs moisture and carbon dioxide as well as air (see some experiments of Bottomley, *Proc. Roy. Soc.*, 38, 158), which form an elastic coating on its surface, and cannot be removed subsequently by any applicable process. The practice of calibrating the tube while open to the air, so generally adopted by the makers, and advocated even by many eminent physicists, will utterly ruin any tube for really delicate work.

I may be excused for drawing attention to one other detail in construction, the observance of which may save a good instrument from being spoilt at the last moment. The graduation of the stem should never be left to the workman's discretion, and should never be commenced without first having a trial made on a waste piece of glass. It is of the greatest importance that the lines should be very fine, regular, and clean cut; but in addition to this they should be very short, and well to the side of the front portion of the stem; the fifth and tenth lines should be only just perceptibly longer than the others, and the figures should be at some distance from the lines. In this way a good view of the mercurial column may be obtained to the side of the graduations, and it is never obstructed by the graduations themselves.

However good a thermometer tube may be, there are generally a few points in it past which the mercury will not move easily, and at which the column will even break off in some cases. These sticking points are caused by some contraction or imperfection in the bore of the tube, too minute to be noticed in the calibration of the instrument; and such points must be sought out, and, if possible, be avoided in any experiments, or, at any rate, the final and initial readings of the instrument should be adjusted so as to be clear of them.*

The calibration correction in the case of both instruments used in the present work was very small considering their length (graduated stem = 400 mm.), and the errors due to such corrections were almost entirely eliminated by the method described previously, of removing some of the mercury into the upper chamber, so that exactly the same portion of the stem should be used for all experiments with the same salt, whatever the actual temperature of the experiment might be. Instead of removing the mercury by heat, a simpler arrangement was after much trouble procured. On to the upper end of the tube, a wider tube was attached, and in this there was a small constriction, or knife-edge, as it is termed technically, sufficiently wide to allow the mercury to pass freely in either direction, but at which the column at once separates if the instrument be swung or jerked. After each adjustment the calorimetric thermometer is compared with the others used in the work (for the temperature of the salt, &c.), and with the standard which gives the value of the initial reading in degrees centigrade. The initial reading of the instrument in each experiment of a series was identical within less than 1 mm.

---

* Further details respecting thermometers will be found in the *Phil. Mag.*, 1886, 180, 330, and 1887.

Methods of Experimenting.

In conducting an experiment, the rate of cooling before the salt is added was practically *nil*, owing to the temperature of the air being the same as that of the calorimeter. It is advisable, however, that it should not be absolutely *nil*: for the motion of the mercury past certain points in the stem not being regular, as mentioned above, more reliance can be placed on any reading where the column is moving slowly but steadily than when it is quite stationary. In each experiment, the thermometer was read once before the initial temperature was finally read, so as to make sure that no sticking of the column had taken place. The rate of cooling necessary is only about 0·001° per one or two minutes, a rate which, for the purposes of calculating the loss during the uncertain interval while the salt is dissolving, may safely be taken as *nil*.

As soon as the thermometer is read, the salt is removed from the water-jacket surrounding it and shaken into the calorimeter; this operation occupies an interval (which we may term A), which may be seen from the experiments quoted above to be very constant in duration (15 secs.); a second interval, B, then occurs, during which the salt is dissolving, the time is then noted, and a third interval, C, equal in duration to A, is allowed. If the initial temperature were read at 0′ 0″, and the end of the interval C occurred at 1′ 0″, the initial temperature was taken as having been read at 0′ 30″, and, in order to obtain the final temperature, the thermometer was read at 2′ 30″, 4′ 30″, 6′ 30″, &c., the rate of cooling thus determined being added on to the first of these readings. In this way the correction for cooling applied to the uncertain interval is half the rate at the final temperature, that is, intermediate between the initial (*nil*) and final rates; the interval C counterbalancing the interval A.

Salts examined.

The previous investigation was confined to metallic sulphates, and for the present one typical salts of other classes were sought. Very great difficulty was met with in procuring suitable substances. In order to obtain great accuracy in the results, the salt must dissolve quickly and without much caking; it must be obtainable in the anhydrous state without decomposition, a circumstance which precludes the use of very many salts (*Chem. News*, 53, 279). Moreover, in order to powder and sift them on a large scale, they must not be very deliquescent or efflorescent; and, finally, the salts sought were those which in their respective classes contained a considerable amount of water, and exhibited considerable differences in their heat of dissolution.

Thirteen salts were finally selected, and 2 or 3 kilos of each were prepared: in helping me with which laborious work, and also with the calculation of a considerable part of the results, I have to thank Mr. P. G. Sanford. It is, for reasons pointed out elsewhere (*Chem. News*, **54**, 277), impossible to prepare most hydrated salts with the exact theoretical percentage of water, this was, therefore, not attempted, and the salts contained generally slightly less than the calculated amount. The preparations were as follows:—

Potassium Chloride.—This salt requires prolonged heating at a low red heat to drive off all the enclosed moisture In order to ascertain whether the temperature of preparation had any effect on the calorimetric results, two samples were dehydrated: the one at the lowest possible temperature, the other at a temperature just below its melting point; these gave on dissolving in 200 H_2O—

No. 3663 lowest temp.	− 4672	cal.	at 13·5°.
„ 3664 highest „	− 4701	„	„
Thomsen found „	− 4597	„	„*
Berthelot „ „	− 4480	„	„

The two preparations were, therefore, identical. That used in the series of experiments (No. 3675) gave −4655 cal. at the same temperature.

Sodium Chloride.—Examined in the same way as the potassium salt, gave—

No. 3665 lowest temp.	− 1355	cal.	at 13·6°.
„ 3664 highest „	− 1361	„	„
Thomsen found	− 1321	„	„
Berthelot „	− 1311	„	„

The sample used in the series of experiments (No. 3674) gave −1366 cal.

Potassium Nitrate.—As this salt melts at 360°, the sample which was prepared at the highest temperature was not heated above 300°, that prepared at the lowest temperature was heated at 100—110°; they gave the following results:—

---

* Deduced from results at 18° and 21·6° respectively; in some cases the temperatures at which Berthelot and Thomsen dissolved their salts are given approximately only.

No. 3661 lowest temp.	— 8514*	cal.	at 13·47°.
„ 3660 highest „	— 8600	„	„
Thomsen found	— 8672	„	„
Berthelot „	— 8352	„	„

Two samples were used in the series of experiments, Nos. 3659 and 3978; they gave —8596 and —8609 cal. respectively at this temperature.

Strontium Chloride, Anhydrous.—The last traces of moisture in this salt could be expelled only by protracted heating in a platinum dish over a rose burner. Two samples prepared at as low and as high a temperature as possible, gave—

No. 3652 lowest temp.	— 10874	cal.	at 13·5°.
„ 3653 highest „	— 10927	„	„
Thomsen found	— 10770	„	„
Berthelot „	— 11300	„	„

The sample used in the series of experiments (No. 3667) gave 10915 cal.

Strontium Chloride, Hydrated, $SrCl_2,6H_2O$.—Some difficulty was experienced in preparing this salt, owing to its being deliquescent. After finely powdering, it was exposed in a vacuum for a few minutes, and then sifted very quickly. On analysis, the sample (No. 3672) gave—

(1.) 40·512 per cent. water.
(2.) 40·510 „ „

Mean.. 40·511 Theory.. 40·542 per cent.;

and hence it contained $5{\cdot}992H_2O$.

On dissolution at 18°, it gave —7545 cal., as against —7500 obtained by Thomsen with a sample containing $6H_2O$, and —7010 obtained by Berthelot.

Strontium Nitrate, Anhydrous.—Prepared in a similar manner to the chloride; two samples gave—

No. 3654 lowest temp.	— 5157	cal.	at 13·51°.
„ 3655 highest „	— 5126	„	„
Thomsen found	— 4943	„	„
Berthelot „	— 5113	„	„

---

* These preliminary experiments were not performed with the delicate thermometers.

The sample used in the series of experiments (No. 3666) gave −5108 cal. at this temperature.

Strontium Nitrate, Hydrated, $Sr(NO_3)_2,4H_2O$.—The preparation of this salt (No. 3668) gave on analysis—

(1.) 25·330 per cent. water.
25·328 „ „
25·338 „ „
Mean.. 25·333 Theory.. 25·394 per cent;

hence it contains $3·987H_2O$.

On dissolution, it gave −12794 cal. at 18°, against Thomsen's preparation with $4·02H_2O$, which gave −12300.

Sodium Carbonate, Anhydrous.—Samples of this salt, prepared at temperatures between 60° and its fusing point, gave identical results, details of which will be found in this vol., p. 72.

Sodium Carbonate, Hydrated, $Na_2CO_3,10H_2O$.—On analysis, the sample (No. 3683) gave—

(1.) 62 826 per cent. water.
(2.) 62·826 „ „ Theory.. 62 920 per cent.;

hence it contained $9·96H_2O$.

On dissolution, it gave −16185 cal. at 18°, against Thomsen's −16160 at the same temperature.

Sodium Acetate, Anhydrous.—Samples were prepared in a vacuum, at 100° and 200°; they gave—

No. 3658 *in vacuo,*	3886	cal. at 13·58°.
„ 3649 at 100°,	3854	„ „
„ 3650 at 200°,	3922	„ „
Thomsen found	3825	„ „
Berthelot „	4185	„ „

Two preparations were used in the series of experiments; No. 3679 gave 3913 cal., and No. 4552 gave 3910 cal. at this temperature.

Sodium Acetate, Hydrated, $NaC_2H_3O_2,3H_2O$.—The sample of this salt (No. 3689) gave on analysis—

(1.) 39 829 per cent. water.
(2.) 39·848 „ „
Mean.. 39·838 „ „ Theory.. 39 704;

so it appeared to contain $3·017H_2O$. As this excess over $3H_2O$ is probably due to the presence of traces of enclosed water, or to a slight amount of decomposition having occurred during the dehydration, it was considered advisable to take the water as being exactly $3H_2O$ in the calculations.

On dissolution at 18°, it gave —4773 cal., against Thomsen's —4810, and Berthelot's —4640 at the same temperature.

Rochelle Salt, Anhydrous.—The hydrated salt was heated at a temperature below 100°; it fused, and after the greater portion of the water had been expelled, and the salt solidified, it was powdered and sifted, and then heated again at about 150° till constant in weight. As a lower temperature was found insufficient to dehydrate it, and a higher temperature induced decomposition, it is not possible to feel certain that the salt was perfectly anhydrous. On dissolution, the sample used in the experiments, No. 3914, gave —2975 cal. at 15°, against —1900 (?) found by Berthelot at the same temperature.

Rochelle Salt, Hydrated, $KNaC_4H_4O_6,4H_2O$ (sample No. 3688).—For the reason first stated it is not possible to rely on the water determinations made with this salt; they were—

(1.)	23·475	per cent.	
*(2.)	23·488	„	
Mean..	23·482	„	= $3·56H_2O$;

which, if right, show a considerable deficit, the theoretical percentage being 25·520. In the calculations, I have assumed that the salt contained the theoretical amount.

On dissolution at —15°, it gave —12520 cal., while Berthelot found —12300.

The sulphates which were examined were prepared in the same manner as in the earlier work (p. 269).

The dehydrated salts were kept in a number of small bottles, each of which contained sufficient for two determinations. The large bottles containing the hydrated salts were kept continually shaken, it being important to avoid caking in the bottle, which is apt to render the contents unhomogeneous.

Series of Experiments.

All the series of experiments were started at 14° with thermometer 65108, the initial reading of the mercurial column being identical in all cases, and experiments were performed at each degree centigrade up to 25°. After this a similar series of experiments at the same temperatures were started at 13°, with thermometer 65561, and carried up to 25°. At temperatures below 13°, experiments were generally done at every other degree only with each instrument, using No. 65108 for the even degrees and 65561 for the uneven ones, and the experiments were thus carried down, as the atmospheric temperatures served, to 3°.

---

* A third analysis gave 24·206, but this may be a simple mistake.

In cases where the series showed irregularities which required further investigation, other fresh series of experiments more or less complete were performed, using for them a totally different portion of the stem of the thermometer; this, I believe, to be in every way equivalent to using a different instrument. Provided the bulb of a thermometer be a good one, all the peculiarities of the instrument are attributable, I feel sure, to the stem. The series performed with different portions of the stem of the thermometers 65108 and 65561 may be conveniently designated as with '08A, '08B, '61C, &c.*

Any experiments which appeared to be exceptional or of doubtful accuracy were repeated, and if not confirmed, were rejected; these, however, amount in all to only 25 (of which 20 were known at the time of their performance to have come entirely to grief) out of a total of 730—a small percentage when it is remembered that work which is dependent on atmospheric temperatures must often be done against time, and that various small circumstances, such as an accidental splash or a sudden draught, &c., may invalidate the results.

As various experiments about 14° were being performed at intervals throughout the duration of the work, these would have afforded evidence in case the sample used had suffered any alterations since the commencement of the work at this temperature. No such alteration, however, was observed in any case.

Explanation of the Tables and Plates.

The proportion of salt to water taken was $1:200H_2O$ in the case of salts of the monobasic acids, and $1:400H_2O$ in the other cases; the actual proportions being $\frac{1}{6}$ and $\frac{1}{12}$ gram-molecule to 600 c.c. of water. An estimation figure (0·05 mm.) of the thermometer corresponds in the former cases to 2·1 and 1·8 cal. according as thermometer '08 or '61 was used, in the latter to 4·3 and 3·6 cal. respectively.

In the Tables A, B, &c., experimental details are given sufficient for the recalculation of any of the results, though in a more abbreviated form than in the previous communication. w is the weight of salt taken, corrected to weight in a vacuum. The water equivalent of the calorimeter and its contents is made up of $601·74 + 0·016\ (T°-4)$ c.c. of water + any water contained in the salt, calculated according to the analytical results (except in the case of hydrated Rochelle salt and sodium acetate, where the theoretical amount was taken as being present) + the water equivalent of the thermometer, stirrer, &c., amounting to 8·099 grams when ’08 was employed and 8·26 grams when ’61 was employed. In the case of hydrated Rochelle salt and hydrated sodium carbonate, and in a few other less important cases, another 0·11 gram must be added for the wire gauze tray which was used. With anhydrous Rochelle salt and with anhydrous sodium carbonate, the total water equivalent is 0·21 and 0·44 gram less respectively, owing to the thermometers being immersed to a smaller depth in the liquid. The total water equivalent amounts roughly to 610 grams with the anhydrous salts, 616 grams with hydrated Rochelle salt and strontium nitrate, 619 grams with hydrated strontium chloride and sodium acetate, and 625 grams with hydrated sodium carbonate.

---

* The actual positions of the mercury at the initial temperatures were '08A = 244 mm.; '08B = 147 mm.; '08D = 367 mm.; '61A = 258 mm.; 61B = 147 mm.; '61C = 58 mm.; '61D = 365 mm., the graduated stem being 400 mm. long.

It has been thought unnecessary to give the temperature of the salt before its introduction into the calorimeter, as this rarely differed by more than 0·05° from that of the water, and its effect on the initial temperature scarcely ever amounted to one estimation figure of the thermometer. The initial temperature t is given in round numbers (to 0·005°) in degrees centigrade, and the rise or fall, $t' - t$ or $t - t'$, is given accurately in like degrees. M represents the molecular heat of dissolution given in one column at the initial temperature t, and in another, for the sake of comparison, at the nearest whole degree centigrade (deduced diagrammatically by joining all the results at t by straight lines). With hydrated salts, M is the corrected heat of dissolution, obtained by subtracting from the observed heat, m, the heat of fusion of the water contained in it, taking the amount given by the analyses (except in the case of Rochelle salt and sodium acetate) and using the numbers given in Plate VII of the former communication, in which paper will also be found further details as to the calculation.

Each series with a different instrument is given separately.

The mean results are collected and discussed in the Tables I, II, &c., given in the text, and are further illustrated in the diagrams. These contain the figure representing the heat of dissolution of the anhydrous salt, the figure representing the "corrected" heat of dissolution of the hydrated salt (called formerly the "true" heat of dissolution), a third figure representing the apparent heat of dissolution of the same, and, lastly, one representing the heat of combination of the solid salt with its water of crystallisation, obtained by deducting the corrected heat of dissolution of the hydrated salt from that of the anhydrous salt.

The method adopted in drawing the curves will be best explained by taking an instance: thus, with potassium chloride (Plate I and Table I, p. 306) the 16 mean results from 10° to 25° inclusive evidently form a straight line; taking the mean of the first eight of these we get —4348 cal. at 21·5°, and of the last eight —4654 cal. at 13·5°; these two points were then plotted down, and the straight line joining them was extended upwards to 25° and downwards till it met the straight line obtained in a similar manner from the experiments below 9°. The mean results taken for this purpose are given in the various cases at the foot of the Tables I, II, &c.

Each small division of the paper represents 25 cal. with salts of the monobasic acids and 50 cal. with those of the bibasic acids.

A higher position on the paper corresponds to a larger evolution of heat or a smaller absorption of heat.

The mean results are deduced from the lines representing the various series, and not from the individual results only; in this way no undue preponderance is given to any one series: for instance, the mean results with potassium chloride at 17° depends on the value given by the series '61A as well as those given by the other series, although no experiment with '61A was done at that temperature, but only at 16° and 18°. In four cases confirmatory experiments at 4° were performed with '08B (*e.g.*, KCl), and as these stood by themselves in their series, only half value has been assigned to them in calculating the mean result at this temperature; in one or two other cases, results of doubtful accuracy were allowed half value only, and this is indicated in the tables by placing such results within brackets.

The points given in the lines representing the heat of combination of the salt with its water of crystallisation are deduced from points in the *mean lines* representing the heat of dissolution of the salt, and not from the position of the actual experiments at those points.

Experimental Results.

Potassium Chloride.—The four series of experiments performed with this salt, together with the resultant mean series, are given in Plate I, and are marked '08A, '61A, &c., according to the thermometer used. The individual series are represented by dotted lines and are plotted for the sake of greater clearness 4, 8, 12, &c., divisions (100, 200, 400 cal.) above their proper position according to the numbers given in the margin; each one, however, is accompanied by a continuous line which represents the mean result in a similar position. The figures in the margin refer only to the curve marked "mean."

Now looking at the portions of the curves with '08A above 13° (those results obtained first), it will be noticed that, in ascending, the line is suddenly shifted up at a certain point. This alteration was at first thought to be real, and in order to investigate it further the two other series '08B and '61B as well as '61A, were performed, but, as they failed to show any similar change, the shifting had to be attributed to some experimental error. This apparent shifting up of the line as the temperature rises is not so marked here as in some other cases to be noticed below, and a similar shifting (in one or two cases downwards) was noticed at some point with many of the salts. It often occurred persistently in the results with both the instruments '08A and '61A at nearly the same temperature, but in every case was found to be illusory when investigated more fully. It was experimental errors of this nature, combined with the comparative incompleteness of the various series, which deceived the author in his earlier work, and which led him to regard the curves or lines as a series of separate curves. For some satisfactory explanation of these sudden shiftings of the curves (generally indicating diminution of the heat absorbed or increase of the heat evolved) he has sought in vain. The height of the barometer, the small variations in the quantity of salt taken, the gases dissolved in the water used, are all possible causes which have been investigated, but found inadequate to afford any explanation. They must perforce be attributed to errors in the thermometers, although this is equally unsatisfactory: the starting point of the mercurial column is the same in each experiment of the whole series, the final point is not; in one case the mercury falls to *t'*, whereas at some higher temperature it will only fall to *t''*; one can only imagine that there exists some point between *t'* and *t''* which tends to make the mercury stick, and that when below this point, at *t'*, it works normally, whereas above it, at *t''*, it is prevented by the obstruction from falling as far as it should. Such sticking points certainly do exist, as has been already mentioned, but the explanation is not satisfactory, for the final temperature is not read when the column is stationary but when moving, and the rate of cooling determined in these cases should exhibit irregularities as the column approaches or recedes from the sticking point; moreover, the rise in the curves occurred in many very different cases (that is, when the final position of the mercury was in all parts of the tube), at nearly the same actual temperatures (at about 18°), although the two series of experiments were performed at very different times; and another objection to such an explanation is that, owing to the slight variation in the weight of salt taken, the column often falls as far as *t'* in the experiment at the *higher* temperature and only as far as *t''* in that at the lower temperature. Whatever be the true cause of these irregularities, they may be obliterated by a sufficient number of experiments with different parts of the instruments, and in their nature are easily recognisable from such variations as, I take it, are really due to variations in the heat evolved on dissolution.

These variations consist, as will be seen at once, of a sudden and well-defined alteration in the inclination of the lines representing the heat of dissolution. A careful inspection of Table I, which contains

TABLE I.—*Potassium Chloride. Mean Results.*

T.°	M, found.	Differences.			M, calculated.	Difference.
25	−4218 cal.				−4210 cal.	+8
24	−4252 „	34			−4248 „	+4
23	−4285 „	33			−4287 „	−2
22	−4323 „	38			−4325 „	−2
21	−4365 „	42	38·0		−4364 „	+1
20	−4403 „	38			−4403 „	0
19	−4441 „	39			−4442 „	−1
18	−4477 „	36			−4480 „	−3
17	−4522 „	45		38·4 (38·6)	−4519 „	+3
16	−4555 „	33			−4558 „	−3
15	−4596 „	41			−4596 „	0
14	−4634 „	38			−4635 „	−1
13	−4674 „	40	38·8		−4673 „	+1
12	−4709 „	35			−4712 „	−3
11	−4750 „	41			−4750 „	0
10	−4791 „	41			−4789 „	+2
9	−4833 „	42			−4828 „	+5
8	−4883 „	50			−4884 „	−1
7	−4936 „	53	50·7		−4934 „	+2
6	−4985 „	49		50·2 (50·0)	−4984 „	+1
5	−5033 „	48			−5034 „	−1
4	−5085 „	52	49·7		−5084 „	+1
3	−5134 „	49			−5134 „	0

Average points for the highest portion, −4345·5 cal. at 21·5° and −4651 cal. at 13·5°, whence increase = 38·6 per degree; ditto for lowest portion, −4909 at 7·5° and 5059 at 4·5°, whence increase = 50 per degree.

the mean results with this salt cannot fail, I think, to carry conviction with it as to the reality of this alteration, and inspire confidence in the results generally. Columns 1 and 2 contain the temperatures and the experimental results. In column 3 the differences between the results at consecutive degrees are given; these arrange themselves into two groups. From 25° to 9°, the increase for a fall of one degree is 38·4 cal., the various numbers ranging from 33 to 42 cal., and as to the uniformity of this increase, and, consequently, the straightness of the line which represents it, there can be little doubt, the increase from 25° to 17° giving an average of 38 cal. per degree, and that from 17° to 9°, 38·8 cal. All these differences, however, depend on the comparison of the results at two points only, and a more accurate number for the rate of increase may be deduced from the average points given at the foot of the table, and inserted in column 3 in brackets.

Below 9° the rate of increase becomes suddenly augmented by 30 per cent., reaching 50 cal. per degree, and remains constant throughout an interval of six degrees, the total increase from 9° to 6°, and from 6° to 3° differing by 3 cal. only.

In column 4 are given the calculated values as deduced from the "average points" by drawing straight lines through them, and continuing them till they meet; and in the last column are given the differences between these calculated values and the observed values. The one result at the extreme point 25° is exceptionally high (only 8 cal., however), and, as a similar excess occurs in the case of sodium chloride, it is probable that the line undergoes another deflection at about 24°; omitting this one result, therefore, it will be seen that the greatest errors amount to 5 cal. in one case, 4 cal. in one case also, and all the others 3 cal. or less; the average error of the 22 results being only 1·7 cal., a quantity which corresponds to somewhat *less than* 0·05 *mm. of the mercurial column, or the two-thousandth of a degree.* It is true that the results with potassium chloride are exceptionally concordant, but the general mean of the similar errors in the whole work amounts to only 3·5 cal. (calculated as for salts of monobasic acids),* or less than the one-thousandth of a degree. This does not, of course, represent the error of single experiments, as each of these points are the result of two or three experiments; but the average divergence of each single experiment from the calculated value is only 7·4 cal., and the average difference between any pair of experiments 11 cal. (both calculated to salts of monobasic acids); a result which cannot be regarded otherwise than satisfactory, especially when it is noted that the greater part of this error results from peculiarities which do not affect the conclusions here drawn, for on looking at Plate I it will be seen that the results obtained with one instrument are often uniformly above the average (*e.g.*, '08A and '61A), whereas those with the others are uniformly below it (*e.g.*, '08B and '61B). This does not affect the inclination of the lines, though it augments considerably the divergence between the actual experiments. A similar fact was observed in nearly all cases, but the higher results were obtained in some with one instrument, in others with the other, according to which salt happened to be under examination. It must be remembered also that all the duplicate experiments in this work were performed under conditions most unfavourable for producing concordance, namely, with different instruments, and at long intervals of time apart.†

---

* The same thermometric quantity represents double the number of calories with salts of bibasic acids.

† The average difference between experiments performed under like conditions in my former work would be 25 cal. See *Phil. Mag.*, 1886, 328.

I have indicated by a line across the tables which formula was used for obtaining the calculated value at the temperature where the change of rate occurs.

Sodium Chloride. Tables II and B, Plate I.—The lines representing the results with sodium chloride are very similar to those with potassium chloride. The result at 25° is considerably below (larger heat absorption) the calculated value, and is probably the beginning of a fresh rate of alteration. The rate of increase with falling temperature, which is rather less than with the potassium salt, alters suddenly at the same temperature (10°) within experimental error, becoming 39 per cent. larger. The average error here is 3·2 cal.

TABLE II.—*Sodium Chloride. Mean Results.*

T.°	M, found.	Differences.			M, calculated.	Difference.
25	−1024 cal.					
24	−1046 ,,	22			−1040 cal.	+6
23	−1075 ,,	29			−1072 ,,	+3
22	−1104 ,,	29			−1103 ,,	+1
21	−1135 ,,	31	29·5		−1134 ,,	+1
20	−1164 ,,	29			−1166 ,,	−2
19	−1193 ,,	29			−1197 ,,	−4
18	−1223 ,,	30		30·7 (31·3)	−1228 ,,	−5
17	−1254 ,,	31			−1260 ,,	−6
16	−1290 ,,	36			−1291 ,,	−1
15	−1327 ,,	37			−1322 ,,	+5
14	−1358 ,,	31	31·7		−1353 ,,	+5
13	−1386 ,,	28			−1385 ,,	+1
12	−1413 ,,	27			−1416 ,,	−3
11	−1445 ,,	32			−1447 ,,	−2
10	−1483 ,,	38			−1478 ,,	+5
9	−1521 ,,	38	38·0		−1520 ,,	+1
8	−1556 ,,	36			−1563 ,,	−7
7	−1597 ,,	41		41·3 (42·4).	−1605 ,,	−8
6	−1648 ,,	51			−1648 ,,	0
5	−1693 ,,	45	44·5		−1690 ,,	+3
4	−1736 ,,	43			−1732 ,,	+4
3	−1775 ,,	39			−1775 ,,	0

Average points for the highest portion, − 1134·3 cal. at 21° and − 1353·3 at 14°, whence increase = 31·3 per degree; ditto for lowest portion, − 1520·4 at 9° and − 1690 at 5°, whence increase = 42·4 per degree.

Potassium Nitrate. Tables III and C, Plate I.—The results with this salt closely resemble those with potassium chloride, except that the break occurs at a higher temperature, 12°, and that there is no indication of any other break at 25°. At the break, the rate of alteration is increased by 32 per cent. The average error is 4·3 cal.

TABLE III.—*Potassium Nitrate. Mean Results.*

T.°	M, found.	Differences.			M, calculated.	Difference.
25	−8220 cal.				−8219 cal.	+ 1
24	−8259 „	39	33·2	33·0 (33·3)	−8253 „	+ 6
23	−8294 „	35			−8286 „	+ 8
22	−8320 „	26			−8319 „	+ 1
21	−8347 „	27			−8353 „	− 6
20	−8376 „	29			−8386 „	−10
19	−8419 „	43			−8419 „	0
18	−8459 „	40	32·7		−8453 „	+ 6
17	−8486 „	27			−8486 „	0
16	−8513 „	27			−8519 „	− 6
15	−8550 „	37			−8552 „	− 2
14	−8592 „	42			−8586 „	− 6
13	−8615 „	23			−8619 „	− 4
12	−8655 „	40	40·8	41·8 (44)	−8649 „	+ 6
11	−8696 „	41			−8693 „	+ 3
10	−8738 „	42			−8737 „	+ 1
9	−8777 „	39			−8781 „	− 4
8	−8819 „	42			−8825 „	− 6
7	−8868 „	49	42·8		−8869 „	− 1
6	−8915 „	47			−8913 „	+ 2
5	−8961 „	46			−8957 „	+ 4
4	−9007 „	46			−9001 „	+ 6
3	−9033 „	26			−9045 „	−12

Average points for the highest portion, − 8319·3 cal. at 22° and − 8519 at 16°, whence increase = 33·3 per degree; ditto for the lowest portion, − 8737 at 10° and − 8956·8 at 5°, whence increase = 44 per degree.

Strontium Chloride. Tables IV, V, D, and E, Plate II.—The results with the anhydrous salt were not very concordant, and show an average divergence from the calculated values of 7·7 cal. (corresponding to 3·8 cal. in the salts previously discussed). The experiments at 3° give abnormally high results, but there can be little doubt but that there is an increase in the rate of change at 8°, amounting to 19 per cent.; the hydrated salt shows a similar increase at the same point, amounting to 21 per cent. With the anhydrous salt, another change of 20 per cent. appears to take place at 13°, above which temperature the rate of increase remains constant up to 25°. I do not feel at all certain as to this break at 13°, not only because the individual experiments with this salt were not very concordant, but also because there is no well-defined break at the same point with the hydrated salt; at a somewhat higher temperature, it is true, 15—16°, a slight change in this direction does occur, the rate altering from 91 8 to 87 5 cal, but this alteration is so small that if it stood by itself, it would not be worth consideration

The average error for the hydrated salt is 5 8 cal

TABLE IV—*Anhydrous Strontium Chloride Mean Results*

T°	M, found	Differences			M, calculated	Difference
25	11818 cal	52			11842 cal	−24
24	11766 ,,	71			11762 ,,	+ 4
23	11695 ,,	87	76 8		11681 ,,	+14
22	11612 ,,	91			11601 ,,	+11
21	11521 ,	87			11520 ,,	+ 1
20	11434 ,	85		76·1 (80 4)	11440 ,,	− 6
19	11349 ,,	88			11360 ,,	−11
18	11271 ,,	82			11279 ,,	− 8
17	11189 ,,	71	75 5		11199 ,,	−10
16	11118 ,,	76			11118 ,,	0
15	11042 ,,	61			11138 ,,	+ 4
14	10981 ,,	105			10977 ,,	+ 4
13	10876 ,,	93			10880 ,,	+ 4
12	10783 ,,	100	96 8 (96 5)		10785 ,,	− 2
11	10683 ,,	92			10688 ,,	− 5
10	10591 ,,	97			10591 ,,	0
9	10494 ,,	93			10494 ,,	0
8	10401 ,,	112			10399 ,,	+ 2
7	10289 ,,	123			10284 ,,	+ 5
6	10163 ,,	121	110 0 (115 3)		10169 ,,	+ 6
5	10042 ,,	122			10053 ,,	−11
4	9920 ,,	69			9938 ,,	−18
3	9851 ,,				9823 ,,	+28

Average points for the highest portion, 11641 cal at 22 5° and 11158 4 cal at 16·5°, whence decrease = 80 4 per degree, ditto for the middle portion, 10880 cal at 13° and 10542 3 cal at 9 5°, whence decrease = 96 5 per degree, ditto for the lowest portion, 10284 at 7° and 9938 at 4°, whence decrease = 115 3 per degree

TABLE V.—*Hydrated Strontium Chloride. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	2527 cal.				2535 cal.	− 8
24	2451 „	76			2148 „	+ 3
23	2356 „	95			2360 „	− 4
22	2268 „	88	86·4		2272 „	+ 4
21	2199 „	69			2185 „	+14
20	2095 „	104		85·7 (87·5)	2098 „	− 3
19	2008 „	87			2010 „	− 2
18	1924 „	84			1923 „	+ 1
17	1831 „	93	85·0		1835 „	+ 4
16	1742 „	89			1747 „	− 5
15	1670 „	72			1660 „	+10
14	1560 „	110			1569 „	− 9
13	1476 „	84	94·0		1477 „	− 1
12	1387 „	89			1385 „	+ 2
11	1293 „	94		93·5 (91·8)	1294 „	− 1
10	1202 „	91			1202 „	0
9	1114 „	88	93·0		1110 „	+ 4
8	1016 „	98			1018 „	− 2
7	910 „	106			913 „	− 3
6	822 „	88	110·0		802 „	+20
5	685 „	137		113·0 (111·4)	690 „	− 5
4	575 „	110	115·0		579 „	− 4
3	476 „	99			468 „	+ 8

Average points for highest portion, 2316 cal. at 22·5° and 1835 at 17°, whence decrease = 87·5 per degree; ditto for middle portion, 1523 at 13·5° and 1156 at 9·5°, whence decrease = 91·8 per degree; ditto for lowest portion, 913 at 7° and 578·7 at 4°, whence decrease = 111·4 per degree. For *m* these points are − 7384 at 22·5°, − 7583 at 17°, − 7715 at 13·5°, − 7874 at 9·5°, − 7985 at 7° and − 8164 at 4.°

Strontium Nitrate. Tables VI, VII, F, and G, Plate III.—With the anhydrous salt there appears to be a break at 21°, when the rate increases by 16 per cent. of its value, and a similar break of 16 per cent. also occurs at the same temperature with the hydrated salt. Another increase of 30 per cent. then takes place at 8·5° with the anhydrous salt, and an increase of 28 per cent. at 9° with the hydrated salt.* As far as the differences given in Table VI are concerned, the break with the anhydrous salt would appear to take place at 7°, but the diagram shows that the junction of the two lines really occurs at a temperature practically identical with that in the case of the hydrated salt.

---

* The experiment at 4° with '08B has been omitted in this case in calculating the mean result at this temperature, on account of its being considerably below the results in the other series, and of there being no other experiments with the same instrument at contiguous temperatures. It entirely confirms, however, the increased rate of alteration at low temperatures.

The average error here is 6 cal. for the anhydrous salt, 5·8 cal. for the hydrated salt.

TABLE VI.—*Anhydrous Strontium Nitrate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	−4348 cal.	49	60·3 (60·5)		−4341 cal.	+ 7
24	−4397 ,,	65			−4402 ,,	− 5
23	−4462 ,,	55			−4463 ,,	− 1
22	−4517 ,,	73			−4523 ,,	− 6
21	−4590 ,,	65	67·5	70·8 (70·5)	−4583 ,,	+ 7
20	−4655 ,,	69			−4648 ,,	+ 7
19	−4724 ,,	57			−4718 ,,	+ 6
18	−4781 ,,	79			−4789 ,,	− 8
17	−4860 ,,	68	69·3		−4859 ,,	+ 1
16	−4928 ,,	54			−4930 ,,	− 2
15	−4982 ,,	98			−5000 ,,	− 8
14	−5080 ,,	57			−5071 ,,	− 9
13	−5137 ,,	58	74·2		−5141 ,,	− 4
12	−5195 ,,	75			−5212 ,,	−17
11	−5270 ,,	85			−5282 ,,	−12
10	−5355 ,,	73			−5353 ,,	+ 2
9	−5428 ,,	80			−5423 ,,	+ 3
8	−5508 ,,	81	88·6 (92)		−5503 ,,	− 5
7	−5589 ,,	98			−5595 ,,	− 6
6	−5687 ,,	98			−5687 ,,	0
5	−5785 ,,	91			−5779 ,,	+ 6
4	−5876 ,,	75			−5871 ,,	+ 5
3	−5951 ,,				−5963 ,,	−12

Average points for the highest portion, − 4402 at 24° and − 4523 at 22°, whence increase = 60 5 per degree; ditto for middle portion, − 4788 6 at 18° and − 5282 at 11°, whence increase = 70 5 per degree; ditto for the lowest portion, − 5595 at 7° and − 5871 at 4°, whence increase = 92 per degree.

Table VII.—*Hydrated Strontium Nitrate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference
25	−6005 cal.	78	65·5 (64·5)		−6013 cal.	− 7
24	−6083 „	64			−6078 „	+ 5
23	−6147 „	61			−6143 „	+ 4
22	−6208 „	59			−6207 „	+ 1
21	−6267 „	77	74·5	75·3 (74·5)	−6268 „	− 1
20	−6344 „	73			−6339 „	+ 5
19	−6427 „	62			−6414 „	+13
18	−6489 „	76			−6488 „	+ 1
17	−6565 „	62	75·3		−6563 „	+ 2
16	−6627 „	71			−6637 „	−10
15	−6698 „	88			−6711 „	−13
14	−6786 „	80			−6786 „	0
13	−6866 „	61	76·0		−6851 „	+15
12	−6927 „	65			−6925 „	+ 2
11	−6992 „	91			−7009 „	−17
10	−7083 „	83			−7083 „	0
9	−7166 „	80			−7158 „	+ 8
8	−7246 „	95	96·8 (95·7)		−7245 „	+ 1
7	−7341 „	95			−7341 „	0
6	−7436 „	94			−7437 „	− 1
5	−7530 „	95			−7532 „	− 2
4	−7625 „	105			−7628 „	− 3
3	−7730 „				−7724 „	+ 6

Average points for the highest portion, − 6078 cal. at 24° and − 6207 at 22°, whence increase = 64·5 cal. per degree; ditto for middle portion, − 6488 at 18° and − 7009 at 11°, whence increase = 74·5 per degree; ditto for lowest portion, − 7341 at 7° and − 7628 at 4°, whence increase = 95·7 per degree.

These points for *m* are, − 12579 at 24°, − 12643 at 22°, − 12790 at 18°, − 13067 at 11°, − 13260 at 7° and − 13443 at 4°.

Sodium Carbonate. Tables VIII, IX, H, and I, Plate III.—Owing to the excessive degree in which the anhydrous salt cakes, and, as a consequence, the length of time required for its dissolution, it was not originally intended to examine this salt; a few experiments (two at every third degree) were subsequently performed, chiefly with a view to the heat of its combination with its water of crystallisation. In spite of the difficulties of dealing with it, the average error is not large (8·2 cal.), and the general results are well borne out by their agreement with those obtained with the hydrated salt. At 19° an increase of 26 per cent. occurs in the rate of alteration, and at 7° there is another much larger increase, amounting to 92 per cent. The experiments are, however, not sufficiently numerous to settle with certainty the exact temperature at which these changes occur. Taking the hydrated salt, the first increase occurs at about 18°, and

TABLE VIII.—*Anhydrous Sodium Carbonate. Mean Results.*

T°.	M, found.	Differences.		M, calculated.	Difference.
25	5852 cal.	3 × 52		—	—
22	5695 „	3 × 54	53·0	5693 cal.	+ 2
19	5533 „	3 × 72		—	—
16	5316 „	3 × 77		5311 „	+ 5
13	5084 „	3 × 57	69·3 (67·2)	5109 „	−25
10	4912 „	3 × 70		4908 „	+ 4
7	4701 „	3 × 129		4706 „	− 5
4	4315 „			—	—

Average points for the middle portion 5311 cal. at 16° and 4807 at 8·5°, whence decrease = 67·2 per degree; decrease for the highest portion = 53 per degree.

TABLE IX.—*Hydrated Sodium Carbonate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	+ 5 cal.	54			+ 14 cal.	+ 9
24	− 49 „	53	60·0		− 49 „	0
23	− 102 „	73			− 112 „	−10
22	− 175 „	61		60·1 (62·9)	− 175 „	0
21	− 236 „	53	60·3		− 237 „	− 1
20	− 299 „	57			− 300 „	− 1
19	− 356 „				− 363 „	− 7
18	− 428 „	72			− 420 „	+ 8
17	− 524 „	96			− 508 „	+16
16	− 573 „	49	83·2		− 596 „	+23
15	− 660 „	87			− 684 „	−24
14	− 772 „	112			− 772 „	0
13	− 862 „	90		85·1 (88·0)	− 860 „	+ 2
12	− 961 „	99			− 948 „	+13
11	−1040 „	79	86·7		−1036 „	+ 4
10	−1122 „	82			−1124 „	− 2
9	−1204 „	82			−1212 „	− 8
		88				
8	−1292 „	108			−1294 „	− 2
7	−1400 „	111			−1401 „	− 1
6	−1511 „	113		103·2 (106·7)	−1507 „	+ 4
5	−1624 „	107			−1614 „	+10
4	−1731 „	77			−1721 „	+10
3	−1808 „				−1828 „	−20

Average points for the highest portion, − 80·3 at 23·5° and − 300·3 at 20°, whence increase = 62·9 per degree; ditto for the middle portion, − 552·2 at 16·5° and − 1080·2 at 10·5°; whence increase = 88 per degree; ditto for the lowest portion, − 1401 at 7° and − 1721 at 4°, whence increase = 106·7 per degree. For *m* these points are − 16286·3 at 23·5°, − 16210·3 at 20°, − 16162·2 at 16·5°, −16172·2 at 10·5, − 16189 at 7° and 16245 at 4°.

amounts to 40 per cent., the second one at 7·5°, amounting to 21 per cent. With the *observed* heat of dissolution it will be seen that it decreases from 25° to 18°, remains constant for the next 12 degrees, and then decreases again.

The average error here is somewhat large (7·5 cal.), as is generally the case with salts containing a considerable amount of water, various sources of error being thereby increased.

Sodium Acetate. Tables X, XI, J and K, Plate V.—No less than five nearly complete series of experiments were performed with this salt, on account of the irregularities exhibited. They are given in full in the Plate, and illustrate well the nature of the errors by which I was misled in my former work. (N.B. the general concordance of the irregularities in the series '08A and '61A between 3° and 17°.) The differences which occur between the experiments are very considerable, and much weight could not be attached even to the mean result

TABLE X.—*Anhydrous Sodium Acetate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	3971 cal.	− 2			3973	− 2
24	3973 ,,	− 4			3974	− 1
23	3977 ,,	2	− 0·8 (−0·8)		3975	− 2
22	3775 ,,	1			3975	0
21	3974 ,,				3976	− 2
20	3960 ,,	14			3968	− 8
19	3948 ,,	12			3958	−10
18	3948 ,,	0			3948	0
17	3938 ,,	10	7·7		3938	0
16	3936 ,,	2			3928	+ 8
15	3931 ,,	5			3917	+14
14	3920 ,,	11		10·6 (10·1)	3907	+13
13	3903 ,,	7			3897	+ 6
12	3887 ,,	16			3887	0
11	3873 ,,	14	13·3		3877	− 4
10	3862 ,,	11			3867	− 5
9	3854 ,,	8 14			3857	− 3
8	3840 ,,	14			3845	− 5
7	3826 ,,	17			3825	+ 1
6	3809 ,,	24	20·5 (19·9)		3805	+ 4
6	3785 ,,	17			3795	−10
4	3768 ,,	25			3765	+ 3
3	3743 ,,				3745	− 2

Average points for the highest portion, 3973·7 at 24° 3975 3 at 22°, whence increase = 0·8 per degree; ditto for the middle portion, 3948 at 18° and 3877 at 11°, whence decrease = 10·1 per degree; ditto for the lowest portion, 3825 at 7° and 3765·3 at 4°, whence decrease = 19·9 per degree.

TABLE XI.—*Hydrated Sodium Acetate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	+ 7 cal.	−12	2·5 (5·7)		+ 15 cal.	+ 8
24	+ 19 „	18			+ 9 „	−10
23	+ 1 „	6			+ 3 „	+ 2
22	− 5 „	− 2			− 2 „	+ 3
21	− 3 „	4	11·3	9·7 (10·6)	− 3 „	0
20	− 7 „	19			− 9 „	− 2
19	− 26 „	− 1			− 20 „	+ 6
18	− 25 „	21			− 31 „	− 6
17	− 46 „	2			− 41 „	+ 5
16	− 48 „	14			− 52 „	− 4
15	− 62 „	20			− 62 „	0
14	− 82 „	1	9·3		− 73 „	+ 9
13	− 83 „	6			− 84 „	− 1
12	− 89 „	9			− 94 „	− 5
11	− 98 „	14			−105 „	− 7
10	−112 „	10			−115 „	− 3
9	−122 „	7			−126 „	− 4
8	−129 „	18	24·2 (25·7)		−130 „	− 1
7	−147 „	24			−149 „	− 2
6	−171 „	33			−175 „	+ 4
5	−204 „	20			−200 „	− 4
4	−224 „	26			−226 „	− 2
3	−250 „				−252 „	− 2

Average points for the highest portion, + 9 cal. at 24° and − 2·3 at 22°; whence increase = 5·7 per degree; ditto for the middle portion = − 30·6 at 18° and − 104·7 at 11°, whence increase = 10·6 per degree; ditto for the lowest portion − 149 at 7° and − 226 at 4°, whence increase = 25·7 per degree. For *m* these points are − 4887 at 24°, − 4847·3 at 22°, − 4771·6 at 18°, − 4666·7 at 11°, − 4606 at 7° and − 4604 at 4°.

were it not that it is well supported by the experiments with the hydrated salt.

The influence of temperature on the heat of dissolution of this salt is much smaller than in any other case examined; from 25—21° it is practically constant, *increasing* even at the small rate of 0·8 cal. per degree with fall of temperature. All the five series are so far concordant that they show no increase from 21° upwards, the rate then alters, a decrease of 10·1 cal. per degree occurring till 8°, when this decrease becomes nearly double, 19·9 cal. With the hydrated salt, we have a similar series of changes, an increase of 85 per cent. (not a large quantity in actual quantities; from 5·7 to 10·6 cal.) occurring at 19·5°, and another increase of 142 per cent. at 7°. The apparent heat of dissolution presents the anomaly (noticed also with sodium carbonate over a shorter range) of an *increase* of heat absorbed with *increase* of temperature.

The average error is 4·5 and 3·9 cal. with the anhydrous and hydrated salts respectively.

Rochelle Salt. Tables XII, XIII, L, and M, Plate VI.—In the series of '61A with the anhydrous salt, which was in this case performed first, the rate of change appeared to be considerably less between 20° and 21°, and also between 16° and 18°, than in the rest of the line extending between 13° and 25°. The experiments with '08A were then performed and confirmed these peculiarities in a marked manner. This, however, was not considered as sufficient proof, and two other short series with '08D and '61D were performed, and they showed perfect regularity between 16° and 21°, while experiments with '08E and '61C gave even a higher rate than the normal between 20° and 21°, reducing the mean results to a straight line within experimental error. This instance serves to illustrate what errors may be made by trusting to an insufficient number of series of experiments. This salt cakes considerably, and at low temperatures dissolves very slowly, the results below 8° are consequently not very

TABLE XII.—*Anhydrous Rochelle Salt. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	−2480 cal.				−2473 cal.	+ 7
24	−2532 „	52			−2525 „	+ 7
23	−2583 „	51			−2578 „	+ 5
22	−2630 „	53	50·8		−2631 „	− 1
21	−2683 „	56			−2683 „	0
20	−2732 „	49			−2736 „	− 4
19	−2785 „	53			−2788 „	− 3
18	−2841 „	56			−2841 „	0
17	−2883 „	42			−2893 „	−10
16	−2928 „	45	51·7	54 (52·6)	−2946 „	−18
15	−2976 „	48			−2999 „	−23
14	−3035 „	57			−3052 „	−17
13	−3095 „	60			−3104 „	− 9
12	−3140 „	54			−3157 „	− 9
11	−3207 „	58	60·6		−3210 „	− 3
10	−3277 „	70			−3262 „	+15
9	−3345 „	68			−3315 „	+30
8	−3398 „	43			−3397 „	+ 1
7	−3484 „	86			−3486 „	− 2
6	−3576 „	92	81·6 (89·1)		−3575 „	+ 1
5	−3685 „	109			−3664 „	+21
4	−3769 „	84			−3753 „	+17
3	−3806 „	37			−3843 „	−37

Average points for the higher portion, − 2683·2 cal. at 21° and − 3157 at 12°, whence increase = 52·6 per degree; ditto for the lower portion, − 3486 at 7° and − 3753 at 4°, whence increase = 89·1 per degree.

TABLE XIII.—*Hydrated Rochelle Salt. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
25	−5778 cal.				−5775 cal.	+ 3
24	−5821 „	43			−5819 „	+ 2
23	−5859 „	38	44·0		−5864 „	− 5
22	−5910 „	51		44 (44·7)	−5909 „	+ 1
21	−5952 „	42	46·3		−5953 „	− 1
20	−5998 „	46			−5998 „	0
19	−6071 „	73			−6066 „	+ 5
18	−6138 „	67			−6129 „	+ 9
17	−6205 „	67			−6192 „	+13
16	−6246 „	41	65·8		−6255 „	− 9
15	−6307 „	61			−6318 „	−11
14	−6393 „	86		63·8 (63·1)	−6382 „	+11
13	−6445 „	52			−6445 „	0
12	−6494 „	49			−6508 „	−14
11	−6561 „	67			−6571 „	−10
10	−6640 „	79	61·8		−6634 „	+ 6
9	−6698 „	58			−6697 „	+ 1
8	−6764 „	66			−6760 „	+ 4
7	−6851 „	87			−6849 „	+ 2
6	−6931 „	80			−6942 „	−11
5	−7047 „	86	87 (93·3)		−7035 „	+12
4	−7140 „	93			−7129 „	+11
3	−7199 „	59			−7222 „	−23

Average points for the highest portion, 5819·8 at 24° and − 5953·3 at 21°, whence increase = 44·7 per degree; ditto for the middle portion, − 6160·8 at 17·5° and − 6570·7 at 11°, whence increase = 63·1 per degree; ditto for the lowest portion, − 6848·7 at 7° and − 7128·7 at 4°, whence increase = 93 3 per degree. For *m* these points are − 12347·3 at 24°, − 12377·3 at 21°, − 12405·3 at 17·5°, − 12652·7 at 11°, − 12792·9 at 7° and − 12965·7 at 4°.

trustworthy, but I think they show an unmistakeable increase of about 70 per cent. in the rate of change, agreeing well with that observed with the hydrated salt. The average divergence from the calculated values is 10 cal.

Besides the increase of 48 per cent. in the rate at 7·5° observed with the hydrated salt, there is also another change at 20° of a similar nature. As some of the results here were not very concordant I have given them in full. They may be summarised thus:—

	25°.	20°.	Increase per degree, 25—20°.	17°.	Increase per degree, 20—17°.
'08A……	−5746	−5995	50	−6223	76
'61A……	−5782	−6018	47	−6216	66
'08D …	−5844 −5814 } 5829*	−5984	29	−6222	79
'61D ……	−5753	−5978	45	−6142 −6159 } 6150*	57
'61E……	−5778	−6012	47	−6214	67
	−5778	−5997	44	−6205	70

In every case, the rate between 25° and 20° is less than between 20° and 17°, but series '61D shows the change but very slightly, while '08D shows it in an exaggerated form. If we take the mean of the whole number of experiments we get 44 and 70 cal. as the two rates, or, if we take the most concordant results only (*i.e.*, omitting the results marked with an asterisk), we get the almost identical numbers 45 and 74 cal. There cannot, I think, be much doubt that there is a change at 20°. The average error here is 7·1 cal.

Having thus found that in all the cases investigated any waviness which appeared at first in the lines representing the results was due to error, but little doubt remained but that this appearance observed in my former work on the sulphates was in like manner erroneous. Two cases, however, were selected for investigation, potassium sulphate and hydrated magnesium sulphate: subsequently a few experiments with anhydrous magnesium sulphate and with both the copper sulphates were added, to settle certain points with reference to the heat of combination with the water of crystallisation.

Potassium Sulphate.† Tables XIV and N, Plate I.—The original results are represented in the Plate by the discontinuous line; this consists of two straight lines‡ inclined to each other at an angle, with a considerable depression at their juncture. The fresh experiments are depicted in the continuous lines and show that this depression was illusory; in another respect, however, they entirely confirm the

---

† With this, and the other sulphates, I have used the same proportions of water as in my previous work, $\frac{3}{40}$ instead of $\frac{1}{12}$th of a gram-molecule of salt to 600 c.c. water.

‡ The lower portion I have drawn straighter than in my first communication. An inspection of the original experiments will show that this is justifiable: both series form straight lines below 11°, but the mean becomes somewhat curved, owing to their not being coincident, and to the preponderance of experiments in one series over those in the other at certain points.

TABLE XIV.—*Potassium Sulphate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
20	−6401 cal.	3 × 85·0	84·7 (85)		−6401 cal.	0
17	−6655 ,,	2 × 86·5			−6656 ,,	− 1
15	−6828 ,,	81·0			−6826 ,,	+ 2
14	−6909 ,,	2 × 90·5	98	98·9 (98·9)	−6910 ,,	− 1
12	−7090 ,,	2 × 105·5			−7100 ,,	−10
10	−7301 ,,	3 × 95 0	99		−7298 ,,	+ 3
7	−7587 ,,	3 × 103·0			−7594 ,,	− 7
4	−7896 ,,	101·0			−7891 ,,	+ 5
3	−7997 ,,				−7990 ,,	+ 7

Average points for the highest portion, −6528 cal. at 18·5° and −6868 at 14·5°, whence increase = 85 cal. per degree; ditto for the lowest portion, −7100 at 12° and −7792 at 5°, whence increase = 98·9 per degree.

previous results. They form two straight lines showing rates of increase of 85 and 98·9 cal. respectively, meeting at 14°; while the earlier experiments, for such portions as conform to straightness, the rates of increase are 82·3 cal. from 27° to 17°, and 105·3 cal. (from 12° to 3°) respectively; or, taking the results obtained with thermometer '83 only (given by a fine continuous line in the Plate), which was used in 23 of the 28 experiments below 12°, the rate for the lower portion is 97·2 cal., a number agreeing more fully still with my present determinations.

Magnesium Sulphate. Tables XV, XVI, O, and P. Plate VII.—The curved nature of the line obtained in the first experiments (the dotted line in the Plate) is proved to be incorrect in this case also. The present experiments, represented by the continuous line, show, in the case of the anhydrous salts, no break from 3° to 17°, the rate of

TABLE XV.—*Anhydrous Magnesium Sulphate. Mean Results.*

T°.	M, found.	Differences.			M, calculated.	Difference.
20·0	20540 cal.	3·0 × 59	87·0	88·3 (88·7)	—	—
17·0	20327 ,,	3·5 × 87			20333 cal.	−6
13·5	20024 ,,	3·5 × 87			20023 ,,	+1
10·0	19718 ,,	3·0 × 90	89·6		19713 ,,	+5
7·0	19447 ,,	4·0 × 89			19446 ,,	+1
3·0	19091 ,,				19092 ,,	−1

Average points for the lowest portion, 20023 cal. at 13·5 and 19269 at 5°, whence decrease = 88·7 cal. per degree.

TABLE XVI.—*Hydrated Magnesium Sulphate. Mean Results.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	7298 cal.	3 × 73 2 × 72 80 } 71 (73·5)	7298 cal.	0
17	7078 „		7078 „	0
15	6934 „		6931 „	+ 3
14	6854 „		6857 „	− 3
12	6705 „	2 × 75 2 × 89 3 × 81 3 × 93 93 } 89 (86·5)	6695 „	+10
10	6527 „		6522 „	+ 5
7	6275 „		6263 „	+12
4	5997 „		6003 „	− 6
3	5904 „		5916 „	−12

Average points for the highest portion, 7188 cal at 18·5° and 6894 at 14·5°, whence decrease = 73·5 cal. per degree; ditto for the lowest portion, 6695·3 at 12° and 6089·5 at 5°, whence decrease = 86·5 cal. per degree. For *m* these points are −3900 at 18·5°, −3956 at 14·5°, −4006 at 12° and −4190 at 5°.

increase being 88·7 cal. per degree, the experiments at 20° show that this rate then diminishes to 59 cal. The results with the hydrated salt are more numerous, and are best represented by two straight lines meeting at 12°, the rate of change above this point being 73·5 cal. and below it 86·5 cal. The experiments, however, are not sufficiently numerous in this case to settle with certainty the exact temperatures at which the change occurs, especially so with the anhydrous salt.

Copper Sulphate. Tables XVII, XVIII, Q, and R. Plate VIII.—The old and new experiments are given in the Plate in the same manner as with magnesium sulphate. The determinations are not numerous, but with both the hydrated and anhydrous salt there appears to be an alteration in the rate, of the same nature as in other cases, at 10—11°. It will be seen that the present results with the anhydrous salt are entirely at variance with those originally obtained

TABLE XVII.—*Anhydrous Copper Sulphate.*

T°.	M, found.	Differences.	M, calculated.	Difference.
20	16095 cal.	3·0 × 58·0 3·5 × 58·6 } 58·2 6·5 × 74 3·0 × 84		
17	15921 „		15921 cal.*	0
13·5	15716 „			
7	15235 „			
4	14982 „			

* Calculated value if in the same straight line with results at 20° and 13·5°.

TABLE XVIII.—*Hydrated Copper Sulphate. Mean Results.*

T°.	M, found.	Differences.		M, calculated.	Difference.
20	5270 cal.	3·0 × 73			
17	5050 ,,	3·5 × 60	66·0	5072 cal.*	−22
13·5	4841 ,,	6·5 × 75			
7	4355 ,,	3·3 × 77	75·6	4350 ,, *	+ 5
4	4123 ,,				

* Calculated values if in the same straight line with the results at 20° and 13·5 and at 13·5° and 4° respectively.

above 10°, the difference at 20° amounting to 300 cal., a quantity which cannot be accounted for by experimental error. In order to examine the cause of this difference, a fresh sample of the sulphate was prepared and dissolved at 20°, but it gave the same results as the first sample did; they were—

No. 4565	16112 16078	16095 cal.
No. 4586	16089 16102	16095 cal.

and showed that the error must have been in the former results. I can only account for it on the grounds that the two samples used now had been desiccated at a higher temperature (360°) than in my previous work (200—250°), and that in driving off the water a certain amount of decomposition occurs, resulting in the liberation of free sulphuric acid, which would not have been expelled at these lower temperatures. These traces of acid might not affect the determinations appreciably at low temperatures, although they did at higher temperatures, owing to the rate of alteration in the heat of dissolution of the acid being very different from that of the salt.

It will be noticed that in every case my later determinations with the sulphates give lower results than were obtained in the earlier work, although these "lower" results imply sometimes a larger thermometric change in the calorimeter, sometimes a smaller one, and it is very difficult to conceive any source of error which should have acted in that direction.

The general nature of the lines given by my former experiments consisted of a curve rising from low temperatures, falling at about 14°, and then another curve starting from this point and falling at about 25°. The majority of these experiments were performed with two thermometers, one used from 3—14° and the other from 14° to 25°, and from this fact it is probable that the peculiarities observed were due to the thermometers, the middle portions of the stems of these instruments giving higher results than either of their extremities. There are many difficulties in the way of accepting such an explanation, but at any rate it argues strongly in favour of the necessity of employing the same portion of the thermometer stem in all series of experiments where great accuracy is required.

One general conclusion may be drawn from a study of the results originally obtained with those sulphates which have not been re-examined here, namely, that the rate of alteration in the heat of dissolution is greater at low temperatures than at high ones (except in the case of the lithium sulphate), a fact which is entirely in accordance with all the present results. Thus dividing the curves into two halves at about 14° we get—

	Rate below 14°.	Rate above 14°.
$MgK_2(SO_4)_2$	192 cal.	167 cal.
$MgK_2(SO_4)_2,6H_2O - 6l_m$	161 ,,	151 ,,
$CuK_2(SO_4)_2$	209 ,,	96 ,,
$CuK_2(SO_4)_2,6H_2O - 6l_m$	176 ,,	98 ,,
Na_2SO_4	85 ,,	56 ,,
$Na_2SO_4,10H_2O - 10l_m$	—	82 ,,
Li_2SO_4	79 ,,	81 ,,

In calculating the numbers, I have omitted the deep indentation with hydrated potassium copper sulphate, and I have taken the anhydrous sodium sulphate results to consist of two perfectly straight lines meeting at about 15°, with which view they agree very well. With hydrated sodium sulphate, the experiments at low temperatures are too irregular to be of any value.

Discussion of the General Results.

Without insisting on the correctness of all the details mentioned above, there can, I think, be little doubt but that the heat of dissolution of salts does undergo sudden changes as the temperature rises, the rate at which heat is developed being lessened at each successive change. The results are far too concordant in themselves to permit of imagining these changes to be merely the result of experimental error, especially when no source of error can be conceived which would come into play so suddenly at certain temperatures and introduce errors exhibiting such regularity. It may be noted also that neither the character of the changes nor the actual temperatures at which they occur, bear any relationship to the heat development in the calorimeter, this varying between the limits of +12000 and −16000 cal.

One point which affords strong confirmation as to the reality of these alterations in the rates is that in nearly every case the alteration is observed at the same temperature with both the anhydrous and hydrated salts, although the actual changes of temperature observed in the calorimeter are so different in the two cases. Sometimes, it is true, there may be a difference of a degree in the temperatures at which the break occurs, but it is very easy to see how such a difference may arise from causes other than mere experimental errors: the actual weight of salt taken in the individual experiments varies, of necessity, within certain limits, and hence the proportion of salt to water is not always the same, moreover $\frac{1}{12}$ (or $\frac{1}{6}$) of a gram-molecule of both salts were always taken and dissolved in the *same* volume of water, whereas, in order to obtain solutions of exactly the same strength, the volume of water used for the hydrated salts should have been less by the amount of water of crystallisation in the salt itself. This source of error was not perceived till too late.

In a few cases, such as hydrated sodium carbonate, anhydrous sodium acetate, and anhydrous Rochelle salt, the results are not incompatible with their being represented by a series of very slight curves, but in the large majority the rectilineal nature of the lines is so unmistakable that such is in all probability the nature of them all.

The first break which occurs in ascending from low temperatures takes place between the somewhat wide limits of 7° and 14° according to the salt examined. The annexed table gives the actual temperatures at which both it and the second break occur, and the thermometric interval between them.

TABLE XIX.

Salt.	1st change.	2nd change.	Interval.
Potassium sulphate..	14 0°	Higher than 27°	>13·0°
„ nitrate ...	12 0	„ 25	>13·0
Sodium chloride.....	10·0	24 ?	14·0 ?
Potassium „	9·5	24 ?	14 5 ?
Strontium nitrate ...	9·0	21	12 0
„ chloride ..	8·0	13 ?	5·0 ?
Rochelle salt........	8 0	20	12 0
Sodium acetate......	7·5	21 (? 19·5°)	13·5 (? 12·5°)
„ carbonate ...	7·0	18	11·0

Where the temperature of the change with the anhydrous and hydrated salts was different, I have adopted that one which was most in accord with the change in the heat of combination of the salt with its water of crystallisation, as given in the diagram at the foot of the Plates. One point of relationship between the temperatures of the two breaks becomes at once apparent, and it is a relationship which increases one's confidence in the trustworthiness of the results, namely, that the higher the temperature at which the first break occurs, the higher also that at which the second occurs. There is but one marked exception to this rule—that of strontium chloride, where, for reasons given above, the second break must be accepted with considerable reservation. The interval between the two breaks varies but little from 11° to 14 5°, and in no case, be it remarked, have more than two breaks been observed in the range of 22° over which the experiments extended.

A further examination of the table shows an unmistakeable connection between the temperature at which the change occurs and the nature of the salt. In the case of all the four salts which exist normally without water of crystallisation, the change takes place at higher temperatures than with any hydrated salt, and the salt where the change occurs at the lowest observed temperature is the one which contains the greatest amount of water of crystallisation—sodium carbonate. Looking at the intervals between the two breaks, it is found that this is greater in the case of the anhydrous salts, and least in the case of sodium carbonate; beyond this, however, any relationship does not appear, except that strontium nitrate, Rochelle salt, and sodium acetate—which contain nearly the same amount of water of crystallisation—show the same interval between two consecutive changes. To the fact that the chlorides of the two alkali metals, the two strontium salts, and the two organic salts come next to each other respectively in the order of temperatures at which the breaks occur, no weight can, I think, be attached. Potassium sulphate is included with the other salts in this table, but the other sulphates do not seem to accord with the general order observed. The only break which each of them exhibited being—

Sodium sulphate at 15°,
Magnesium sulphate at 12° (? 17°),
Copper sulphate at 10·5°;

little weight, however, can be attached to these temperatures.

In Table XX (p. 326) the various salts are arranged according to the increase (in calories) in the rate which occurs at the lowest break, the percentage increase, as well as the increase at the higher break (where there is one) is also given. Another column contains the actual rate of change at 15°, and after that comes the corrected heat of dissolution of the salt* and its heat of combination with 1 mol. of water of crystallisa-

---

* The true heat of dissolution of the hydrated salt would be this "corrected" heat plus the heat of fusion of the anhydrous salt, at present an unknown quantity.

TABLE XX.

Salt.	Increase in rate at lowest change.		Increase at highest change. Cal.	Rate at 15°.	Corrected heat of dissolution at 15°.	Heat of combination with each H_2O.
	Percentage.	Cal.				
Potassium copper sulphate	98	23·8	—	24·3 cal.	−1150 cal.	2330 cal.
Sodium acetate	142	15·1	4·9	10·6 „	− 62 „	1330 „
Rochelle salt	48	15·1	9·2	31·6 „	−3659 „	830 „
Sodium sulphate	54	*14·5	—	*28·0 „	*−1785 „	330 „
Potassium sulphate	28	12·0	—	42·5 „	−3110 „	—
„ chloride	30	11·4	—	38·6 „	−1596 „	—
Sodium chloride	39	11·1	—	31·3 „	−1322 „	—
Potassium nitrate	32	10·7	—	33·3 „	−8552 „	—
Strontium „	28	10·6	5·0	37·3 „	−3256 „	430 „
„ chloride	21	9·8	(2 2)	45·9 „	+ 830 „	1570 „
Sodium carbonate	21	9·4	12·6	44·0 „	− 342 „	600 „
Magnesium sulphate	16	6·0	—	36·8 „	+3415 „	1890 „
Copper sulphate	14	4·7	—	33·0 „	+2465 „	1810 „
Potassium magnesium sulphate	11	4·5	—	39·8 „	− 275 „	2020 „

* The actual values are halved in the case of salts of bibasic acids in order to make them comparable with salts of monobasic acids. Similarly with the double sulphates the values are divided by 4.

tion. Between these last two quantities and the rate of change with temperature, or the increase of this rate, there appears to be no connection. In examining the increases in the rates at the two points where alterations occur, it will be seen that the alteration is greater at the lower break than at the higher one; the only exception being sodium carbonate.*

Taking the increase in calories at the lowest break (which is more trustworthy than the higher break), it will be observed that it is the same in both the organic salts, and greater with them than in any case, except the doubtful instance of potassium copper sulphate. The four anhydrous salts also come next to each other in the series, potassium and sodium chloride being very near together. The two nitrates of potassium and strontium exhibit an identical increase, while the two most highly hydrated salts show the smallest increase of any. The actual rate of change does not appear to influence the extent to which the rate is altered, though it may be noted that in the two salts other than sulphates, where the alteration is least, the rate attains the highest proportions.

Here, again, little value can be attached to the results with the sulphates, but it is noticeable that those two hydrated ones which were most thoroughly examined, as well as potassium magnesium sulphate, exhibit an increase in rate far less than in any other case.

To sum up: the chief factors influencing the extent of the changes in the heat of dissolution of a salt, the temperature at which they occur, and the frequency of their occurrence, would appear to be the nature of the non-metallic portion of the salt, and the extent to which the salt combines with water; a much larger number of instances, however, would be requisite to establish this relationship with any degree of precision.

In my previous communication, I interpreted the irregularities which I imagined occurred in the heat of dissolution of a salt by the development of additional heat as the temperature rises, due to the formation of higher hydrates. The present results may be interpreted in a similar manner, but it is equally possible to explain the changes in a diametrically opposite manner. A prolongation of the circumstances existing, say in the case of potassium chloride, between 3° and 8°, would give a larger heat of dissolution for the salt at temperatures above 8° than that which is observed, that is, at these *higher* temperatures some alteration has occurred *absorbing* heat. But, on the other hand, prolonging the conditions existing between 25° and 8° downwards to lower temperatures, we find that the heat of dissolution should be greater than it is, that is, as the temperature *falls* changes involving *absorption* of heat occur. The rectilineal nature of the lines permits, however, of settling between these opposite explanations.

---

* For these numbers I take the heat of dissolution of the *hydrated* salt, as that of the anhydrous salt may be complicated by alterations in the heat of combination of this salt with water of crystallisation. Taking *anhydrous* sodium carbonate, the increase of the lower break is greater than that at the higher break, the numbers being 10·9 and 7·1 cal. respectively.

The increase in the heat of dissolution of a salt with rise of temperature is an inevitable consequence of the specific heat of the solution being less than the sum of the specific heats of its components, the anhydrous salt and water, and the greater this difference is the greater will be the increase in the heat of dissolution of a salt produced by rise of temperature. In every case the change which occurs consists in the sudden lowering of this rate of increase as certain higher temperatures are reached, that is, the difference between the specific heat of the solution and the sum of those of its components becomes suddenly diminished; such a diminution implies *decomposition* and not *combination;* the sudden alterations are, therefore, due to successive simplification of the particles constituting the solution.

The bearing of these observations on the nature of dissolution is of considerable importance. If dissolution be but the result of a purely physical attraction of the salt for water, involving no combination of a chemical nature, that is, in which a certain definite number of molecules are concerned, it is obvious, I think, that a rise of temperature could produce alterations of a uniform nature only. Sudden alterations are characteristic of changes in the component particles of a complex structure, exemplified by the re-arrangement of atoms in molecules (ordinary chemical change), or the re-arrangement or aggregation of a large number of molecules themselves (changes in state from liquid to solid, &c.). The changes here may consist either of the diminution of the degree of hydration of the dissolved salt, or in a reduction of the number of the molecules which are united to form those complex aggregates, which are probably the acting units of which liquids are composed (comp. *Chem. News*, **54**, 215).

Between those ranges of temperature where the heat of dissolution of a salt is represented by a straight line, the specific heat of the solution will of necessity remain constant. At the points where the rate of increase of the heat of dissolution is lowered, the specific heat of the solution will be increased.* No experiments have yet been made which would show that the specific heat is constant through certain small ranges of temperature, but the well-established fact that for considerable ranges it is higher at high than at low temperatures, agrees well with the present observations; these observations, indeed, affording an explanation of the fact.

---

* The specific heat of water and of the salt being practically constant within these small ranges, that of the solution only need be considered.

Tilden's experiments on this same subject (*Proc. Roy. Soc.*, **38**, 401) would appear to bear out the conclusion that the rate at which the heat of dissolution of a salt is influenced by the temperature, is diminished as the temperature rises, and, if correct, would tend to show that further changes occur at temperatures higher than those reached in my work. Thus:—

	Pickering.		Tilden.
Rate with sod. sulphate ..	2—15°	15—25°	32—64°
	85 cal.	56 cal.	25 cal. (sample C)
„ pot. sulphate ..	3—14°	14—27°	15—45°
	99 cal.	85 cal.	17 cal.
„ pot. nitrate....	3—12°	12—25°	15—53°
	44 cal.	33 cal.	11 cal.
„ sod. carbonate..	4—19°	19—25°	22—52°
	67 cal.	53 cal.	22 cal.

Tilden's result, however, must, I venture to think, be accepted with considerable reservation for the following reason:—The principle connecting the heat developed in any chemical reaction with the specific heats of the reagents and product was first enunciated by Person in the equation $Q_T = Q_t + (U-V)(T-t)$ (Q being the heat evolved at T and t, and U and V the specific heat of the reagents and compound respectively), and is accepted on all hands as necessarily true, and as one of the fundamental principles on which thermochemistry depends; indeed if it were not true, if $Q_T < Q_t + U - V$, we should have a creation of energy, and by continually repeating a series of operations (in this case, for instance, dissolving the salt at t, heating the solution to T, crystallising out the salt, and cooling it and the water again to t), perpetual motion would be produced. Now Tilden certainly recognises the obvious truth of Person's principle, and indeed (p. 406) accepts it as applied to the question of dissolution itself; yet the whole object and the chief result of his paper is to prove that it is not applicable. In the case of each salt examined, he arrives at the conclusion that $Q_T < Q_t + U - V$. This result is impossible: either the values he obtains for Q_T and Q_t (heat of dissolution) are incorrect, or the values taken for U and V (the specific heat of salts and solutions given by Kopp and Marignac) are incorrect. Q_T *must* be equal to $Q_t + U - V$.*

---

* The only case in which the observed value for Q_T could differ from that calculated from Q_t and the specific heats, would be if the solution obtained by dissolving the salt at the higher temperature T was not identical with that obtained by

As both Marignac's and Kopp's determinations of the various specific heats are too concordant to permit us to imagine that they contain an error of a magnitude sufficient to account for the difference in the values calculated and found for Q_T, we must necessarily suppose that the error occurs in Tilden's experimental numbers, a supposition which will appear more probable on a closer examination of his results. When his determinations with potassium sulphate, for instance, are compared with those of other physicists, we find—

	Heat of dissolution at 15°.		Increase per degree from 15—24°.
†	— 6956* cal.	(Favre)	—
	— 6826 „	(Pickering)	85 cal.
	— 6636 „	(Thomsen)	73 „
	— 6580 „	(Berthelot)	
	— 5338 „	(Tilden)	18 „

indicating an error amounting to 1200 or 1300 cal. In like manner, his results with potassium nitrate, judged by comparison with the mean deduced from those of Thomsen, Berthelot, Favre, and myself, is roughly 500 cal. too low, with hydrated sodium carbonate 500 cal. too low, and with hydrated sodium sulphate 900 cal. too low. Where errors of such magnitude occur in his experiments at the ordinary atmospheric temperature, 15°, it would be useless to attach any value to the conclusions drawn from experiments at higher temperatures, where the difficulties are increased tenfold, especially as these conclusions depend on differences not greater (94 to 1200 cal.) than the errors observed in those determinations which should be most accurate.

Setting aside, then, Tilden's direct determination of the heat of dissolution of salts at temperatures above 25°, our only means of obtaining any light on the subject will be from the specific heats of their solutions at these temperatures.

---

heating a colder solution up to T. Such a view, however, can hardly be suggested, and is not even hinted at by Tilden.

† There is some uncertainty about the temperature and degree of dilution in Favre's experiment. Berthelot quotes a determination by Chodin as identical with his own and Thomsen's, and also one by Graham giving −6600 cal.

My own results in the case of all the normally anhydrous salts give somewhat higher numbers than those of Berthelot and Thomsen, due partly to my having generally employed a larger proportion of water than they did, and partly to the special precautions which I took to deprive the specimens of all traces of enclosed water.

The actual proportion of water used by Tilden was 100 H_2O, whereas the other physicists used 200 or 400 H_2O; the smaller proportion of water would entail a smaller absorption of heat on dissolving the salt, though the reduction could scarcely amount to the 1200 or 1300 cal. which Tilden's results indicate. An experiment, The quantity U − V gives the difference between the heat of dissolution at temperatures 1° apart, that is, the rate of increase in the heat of dissolution. In Table XXI (p. 332), values for this quantity are given for various degrees of dilution, and for two ranges of temperature, as calculated from the results of Marignac (*Ann. Chim. Phys.* [5], 8, 416). My own direct determinations of the rate are also inserted in the table, and are distinguished by (P). Unfortunately, Marignac did not extend his observations to solutions as dilute as those employed by myself (except in the case of sodium chloride), so that our results are not strictly comparable, but it may be inferred from an examination of his results with stronger solutions, that the rate which he would have found for solutions of same strength as those used by myself would have been 5 or 10 cal. larger (with salts of mono- and bi-basic acids respectively) than the rates with the strongest solutions which he used; these probable values I have inserted in the table in brackets, and it will be seen that they confirm in a very marked degree my own direct determinations.

In drawing any conclusions as to the rates at higher temperatures given by Marignac's determinations, we must, as he expressly states (p. 420), take the general bearing of the results only, and not attach much importance to the values obtained in each individual case; on the whole, however, it seems certain that the rate of increase is lower between 20° and 50° than at lower temperatures, indicating that further changes do occur beyond those here noticed; that the magnitude

however, was performed at 15° in which the proportion of water taken was 100 H_2O, and the value obtained for the heat of dissolution was −6183 cal. This, however, did not represent the whole absorption, for it was found that some of the salt had remained undissolved in spite of the experiment having lasted as long as 23 minutes, the stirrer having been worked rapidly throughout, and notwithstanding that the salt had been previously sifted through the finest silk. In the experiment, the temperature of the liquid fell to 11·7°, and according to Kopp's determination, a saturated solution at this temperature contains 10·4 parts of salt to 100 of water, whereas a solution of K_2SO_4 in 100 H_2O would contain 9·7 of the salt, that is, it would be very nearly saturated: it is difficult to understand how Tilden could have obtained such a solution of such a difficultly soluble salt, unless he had allowed a length of time for the operation quite inconsistent with obtaining results having the least pretensions to accuracy; it would be legitimate to suggest that he may have omitted to notice that some of the salt remained undissolved in this case, were it not that his results at higher temperatures, when the solubility is considerably greater, show a still larger error when compared with those of Berthelot, Thomsen, and myself.

A second attempt to determine the heat of dissolution in 100 H_2O gave the same results, but, by determining the amount of salt which had been dissolved, as well as the rate of cooling by a blank experiment performed immediately afterwards, a fairly trustworthy value was obtained: it was −6316 cal., a number smaller than those obtained with the weaker solutions, but still showing an excess of 1000 cal. over that given by Tilden.

TABLE XXI.—*Rate of Increase of the Heat of Dissolution with Rise of Temperature.*

Salt.	Proportion of water.					Temperature.
	$25H_2O$.	$50H_2O$.	$100H_2O$.	$200H_2O$.	$400H_2O$.	
KCl........	27	31	36	(41), 39 (P)	—	17—22°
	25	30	34	—	—	20—51
NaCl	17	23	30	(35), 31 (P)	—	16—20
	16	21	24	—	—	22—52
$SrCl_2$.......	—	57	68	75	(85), 81 (P)	21—26
	—	55	66	77	—	19—51
$Sr(NO_3)_2$....	—	—	47	55	(65), 61 (P)	21—26
	—	30	47	58	—	19—51
KNO_3	15	22	30	(35), 33 (P)	—	18—23
	14	19	21	—	—	22—52
Na_2CO_3	—	17	36	42	(52), 53 (P)	21—26
	—	13	28	33	—	21—52
$NaC_2H_3O_2$ ..	−13	− 8	+ 2	(7), 1 (P)	—	20—25
	−15	−10	− 7	—	—	19—52
K_2SO_4......	—	—	65	75	(85), 85 (P)	18—23
	—	—	54	63	—	22—52
$MgSO_4$	—	44	55	75	(85), 59 (P)	19—24
	—	40	54	74	—	22—52
$CuSO_4$......	—	37	48	56	(66), 58 (P)	18—23
	—	26	36	46	—	22—53

of these changes, however, is probably less at the higher temperatures, for the greatest decrease in the rates observed does not exceed 12 cal. in this interval of 30°. That the change should be less marked as the temperature is higher, is strictly in accordance with my own observations in those cases where two changes were noticed.

Water of Crystallisation.

The heat of combination of the solid salt with its water of crystallisation (solid) is the difference between the heat of dissolution of anhydrous and hydrated (corr.) salt. The result is given diagrammatically at the foot of each Plate, the marked points showing the values deduced at various temperatures from the straight lines given by the heat of dissolution, and not from the mere experimental results at those temperatures.

In drawing any conclusion as to the variation of the heat of combination of the salt with its water, it must be remembered that its value is given by the combination of two independent quantities, and that the errors made may be considerable unless these conclusions be of a general nature only.

Although any sudden change which occurs in this value can occur only at the temperature where the rate of increase of the heat of dissolution alters, an alteration in this latter rate is by no means always accompanied by a change in the solid crystallised salt. In about one-half of the cases here investigated, the change in the conditions of the salt when dissolved is not accompanied by any change in the solid hydrated salt. Thus although the rate of increase of the heat of solution of the nitrates of strontium is twice lowered between 3° and 25°, the heat of combination of $Sr(NO_3)_2 + 4H_2O$ is represented by a straight line throughout. Nearly every table exhibits instances of a similar character.

Between the limits of 3° and 25° there is certainly a general tendency for the heat of combination to decrease; although the decrease is not large. The total decrease in the various cases is—

Sodium carbonate............	165 cal.
Rochelle salt.................	100 „
Strontium chloride	95 „
„ nitrate	95 „
Sodium acetate	30 „

With strontium nitrate, and possibly with sodium acetate, this decrease is continuous throughout the whole 22° range, but in the other cases it is more or less confined to the higher temperatures, the rate of decrease per degree is consequently greater in these cases than would be given by dividing the above total decrements by 22. The rates are—

$Na_2CO_3,10H_2O$	14·7 cal.	per	degree	7—25°
$SrCl_2,6H_2O$	9·5	„	„	10—25
$NaKC_4H_4O_6,4H_2O$......	8·5	„	„	8—20
$Sr(NO_3)_2,4H_2O$	4·3	„	„	3—25
$NaC_2H_3O_2,3H_2O$	4·5	„	„	21—25

The general order of the rate of decrease is according to the amount of water contained in the salt, and this affords some confirmation of the correctness of the observed values, but they must still be accepted with considerable reservation. With sodium carbonate, the decrease is less above 17° than it is between 17° and 7°, but the difficulties attending the examination of the anhydrous salt render it impossible to attach much value to this apparent change at 17°. Again, with sodium acetate, an increase of the rate of diminution above 21° is very doubtful, and the whole line between 3° and 25° may well be perfectly straight; if we take the exact course indicated by the plotting in this case, the heat of combination from 21° to 8° is absolutely constant, while from

8° to 3° there is a slight rise. With Rochelle salt, the rise at the higher temperatures, 20—25°, is altogether exceptional, and from the paucity of experiments with the anhydrous salt in this region, cannot be regarded as well authenticated.

In two cases, there is a marked diminution in the heat of combination as the lower temperatures are attained, thus with—

Sodium carbonate, decrease from 7—4° = 70 cal., or 23 cal. per degree;
Strontium chloride, decrease from 13—3° = 50 cal., or 5 cal. per degree;

while with Rochelle salt, the increase, which was 8·5 cal. per degree down to 8°, becomes reduced at that temperature to 3 cal. per degree; the actual plottings, also, with strontium nitrate indicate a change in the same direction below 7°, but it is too small to be relied on. Here again the sharpness of the decrease at low temperatures follows the order of the degree of hydration of the salt. It is not difficult to understand how a diminution in the heat of combination of the salt with its water may occur at temperatures which are not far removed from those at which the water molecules present would, if free, aggregate together, and assume a crystalline form peculiar to themselves. This tendency to unite with each other would, as soon as it began to be appreciable, loosen the energy with which they were attached to the salt, and the greater the number of water molecules present the greater would be the effect thus produced, as is indicated in the present results.

The general tendency above 7° or 8°, however, is towards a diminution in the heat of combination as the temperature rises, and as precisely the opposite conclusions were deduced from my previous work on the sulphates, the cases of the copper and magnesium salts were re-examined. The rapid rise in the case of the copper salt was found to be entirely erroneous, owing to the wrong values obtained for the heat of dissolution of the anhydrous salt. The present results indicate a resemblance to the conditions found with the other salts, there being an increase from 4° up to 10°, followed by a decrease as the temperature rises to 20°. This alteration, however, must be looked upon as very uncertain, the actual experiments, shown here by crosses, indicate no appreciable change between 7° and 17°. The increase previously observed in the case of magnesium sulphate is confirmed to a certain extent by the more recent results. The heat of combination increases by 80 cal. from 3° to 17° (the highest temperature noticed in any case at which the heat of combination is increasing), but above that point it begins to decrease rapidly, instead of showing a small further increase, as this decrease, however, depends on determinations at 20° only, it must not be insisted on; similarly with the change at 12°. My former results on this point with other salts cannot, of course, be accepted as being of any appreciable value; it may be observed, however, that the results with potassium copper sulphate are in accordance with my present work, there being an increase in the heat of combination from low temperatures up to 13—15°, after which there is no further increase; and so also with sodium sulphate, the rapid decrease noticed between 16° and 25° is analogous to that noticed in the case of the other highly hydrated salt, sodium carbonate.

Conclusion.

The main results arrived at in the present work may be briefly summarised as follow:—

1. The heat of dissolution of a salt increases uniformly with the temperature up to a certain point, when the rate of increase is suddenly lowered, and this fresh rate continues uniform till lowered again at some higher temperature.

2. These sudden alterations in the rate indicate the occurrence of some fresh heat-absorbing action, as the temperature rises; this action may be the decomposition of some hydrate in solution, or the simplification of the aggregates constituting the true molecules of the solution.

3. As far as the present experiments extend, it would appear that the temperature at which the first alteration in the rate occurs is lower, and the successive alterations are more frequent, according as the salt is more highly hydrated in the normal solid condition.

4. The alterations at higher temperatures are of smaller magnitude than those at lower temperatures.

5. The rate at which the heat of dissolution is found to increase with the temperature is confirmed by the results deduced for the specific heats of the solutions, and these indicate that further alterations in the rates occur at temperatures between 25° and 50°. Tilden's direct determination of the rates in certain cases at these higher temperatures must be regarded as doubtful, since they are entirely at variance with the specific heats.

6. The heat of combination of a solid salt with its water of crystallisation would appear to be diminished by a rise of temperature, the diminution being more marked as the amount of water present is greater. At low temperatures, the reverse is the case, the effect of temperature being, probably, more than counterbalanced by the tendency of the water molecules to leave the salt in order to combine with each other. In the most highly hydrated salts, this diminution with fall of temperature is most apparent.

It has been objected that it is improbable that the molecules of solids and liquids should undergo changes in their constitution at every few degrees, as is shown by the present work; but we certainly have very little grounds on which we can consistently maintain such a view. Of the constitution and complexity of solid and liquid molecules we know nothing, their percentage composition alone is known to us; and till we have some knowledge, however slight, of what these unknown units may be, I venture to think we should be content to investigate, without entering into any useless discussion of probabilities.

Additional Note.—In the discussion which followed the reading of this paper Dr. Wright suggested that the lines representing the heat of dissolution of the salts might in reality be curves represented by formulæ such as $1 + \alpha t + \beta t^2$, instead of being combinations of straight lines. I have consequently examined some of my results in accordance with this suggestion. With potassium chloride, two curves were calculated, taking the experiments at 3° and 6° as origins, and deducing the values of α and β from four and three other pairs of experiments in the series; these two curves were then combined into one, and all the values given by it altered to the extent necessary to render the sum of the negative and positive errors of the observed values equal. The equation for this curve was:—

$$M = -5123 + 48{\cdot}05\,(t-3) - 0{\cdot}315\,(t-3)^2,$$

and the differences between the values calculated from it and the observed values at each successive degree were as follows:—

25°.	24°.	23°.	22°.	21°.	20°.	19°.	18°.	17°.
− 4	− 2	− 3	− 1	+ 5	+ 6	+ 7	+ 3	+ 10

16°.	15°.	14°.	13°.	12°.	11°.	10°.
− 5	+ 6	+ 3	0	− 8	− 6	− 12

9°.	8°.	7°.	6°.	5°.	4°.	3°.
− 14	− 9	− 2	+ 1	+ 3	+ 6	+ 11 cal.

Now the average of these differences is 5·1 cal., a quantity three times larger than that given on the supposition that the results are represented by two straight lines (Table I); but that which tells far more strongly against the curvilinear nature of the results, than the mere increase of the average error which it would entail, is the arrangement of the errors according to their signs; instead of the positive and negative errors occurring indiscriminately, as they do in Table I, they are here arranged in groups, the observed results being uniformly above the curve throughout certain intervals, and uniformly below throughout others, the arrangement, in fact, is exactly what would follow from the observed results being made up of two straight lines meeting at 9° or 10°; and that such, and not a curve, is their nature, is, I think, thus proved beyond question.

Taking the results at 15 points in the case of hydrated strontium nitrate, the equation obtained was $M = -7724 + 95\,8(t - 3) - 0{\cdot}83(t - 3)^2$, and the differences between the values given by this equation and the observed results from 25° downwards were—

− 14, + 4, + 2, + 4, + 1, + 8, + 21, + 14, + 21, + 10, + 4,
+ 16, + 11, 0, − 16, − 10, − 13, − 20, − 14, − 9, − 7,
− 8, + 6,

the distribution of the signs of these differences showing clearly that the curve is inapplicable, while an attempt to apply it raises the average error from 5 8 to 10 1 cal.

With sodium chloride, the application of a curve represented by $M = -1772 + 42\,1(t - 3) - 0{\cdot}36(t - 3)^2$ raises the average differences from 3 2 to 5·4 cal., the signs of the differences being arranged in a manner closely resembling those with strontium nitrate. With potassium nitrate, the formula $M = -9047 + 46\,3(t - 3) - 0\,41(t - 3)^2$ increases the grouping together of differences of like signs, but does not increase the average difference much, namely, from 4·3 to 5·8 cal. only.

With hydrated sodium acetate, where the differences given in Table XI are higher than the average, the curve equation obtained was $M = -234 + 18{\cdot}35(t - 3) - 0{\cdot}315(t - 3)^2$, which gave the differences from 25° downwards as being—

+ 11, − 6, + 6, + 6,
− 3, − 6, + 5, − 4, + 8, 0, + 2, + 12, + 1, − 5, − 8, − 7, − 12,
− 19, − 17, − 10, + 7, + 9, + 16.

Here the results obtained at the higher temperatures might be expressed by the curve, but those at lower temperatures are clearly not expressible in such a manner, indeed from 21° downwards the sign of the differences follows exactly the order which would be produced by two straight lines meeting at about 8° and cutting the curve at three points. The application of this curve would double the average error of the observed results from 3·9 to 7 8 cal.

With hydrated sodium carbonate, the equation obtained was $M = -1827 + 109\,85(t - 3) - 1{\cdot}195(t - 3)^2$, which gave the differences from 25° downwards to be—

+ 3, + 1, − 6, + 4, − 5,
− 14, − 19, + 7, − 26, − 18, + 11, + 14, + 28, + 19, + 7, − 6,
− 16, − 9, + 2, + 11, + 10, − 19,

the average of which is 11·7 cal. instead of the 7·5 cal. given by representing the results by three straight lines, while the arrangement of the positive and negative differences is on the whole such as would be produced by three straight lines cutting the curve.

Thus, in every case which has been investigated it is found impossible to express the experimental results by means of a curve with anything like the same degree of accuracy as they can be by two or three straight lines; the latter, then, is evidently their nature.

TABLE A.—*Heat of Dissolution of Potassium Chloride.* KCl = 74·40; $\frac{1}{12}$ *mol.* = 12·600 *grams.*

w.	*t*°.	$(t-t')$°.	M at *t*.	M at T. Whole degrees C.
Series with Thermometer '08 A.				
1. 12·644	24·96	1·1701	−4201 cal.	−4200 cal. at 25°
2. 12·657	23·92	1·1828	−4242 „	−4240 „ 24
3. 12·678	22·85	1·1940	−4275 „	−4273 „ 23
4. 12·594	21·985	1·1955	−4309 „	−4308 „ 22
5. 12·601	20·895	1·2074	−4349 „	−4346 „ 21
6. 12·650	20·05	1·2224	−4386 „	−4388 „ 20
7. 12·620	18·82	1·2315	−4429 „	−4422 „ 19
8. 12·650	17·93	1·2423	−4457 „	−4454 „ 18
9. 12·682	17·07	1·2623	−4522 „	−4524 „ 17
10. 12·627	16·005	1·2676	−4556 „	−4556 „ 16
11. 12·671	15·005	1·2809	−4588 „	−4588 „ 15
12. 12·610	14·03	1·2864	−4630 „	−4630 „ 14
13. 12·603	12·01	1·3054	−4697 „	−4697 −4717 } −4707 „ 12
14. 12·538	12·05	1·3024	−4714 „	
15. 12·620	10·01	1·3318	−4789 „	−4789 „ 10
16. 12·611	8·00	1·3565	−4881 „	−4881 „ 8
17. 12·593	5·965	1·3835	−4985 „	−4984 „ 6
18. 12·651	3·925	1·4175	−5084 „	−5080 „ 4
19. 12·631	3·08	1·4270	−5126 „	−5129 „ 3
Series with Thermometer '61 A.				
20. 12·621	23·89	1·1835	−4258 cal.	−4254 cal. at 24°
21. 12·648	21·895	1·2064	−4325 „	−4320 „ 22
22. 12·639	19·98	1·2251	−4401 „	−4401 „ 20
23. 12·622	18·02	1·2437	−4473 „	−4474 „ 18
24. 12·622	16·93	1·2559	−4517 „	−4514 „ 17
25. 12·671	15·935	1·2688	−4546 „	−4544 „ 16
26. 12·675	15·00	1·2831	−4596 „	−4596 „ 15
27. 12·700	14·00	1·2945	−4628 „	−4628 „ 14
28. 12·613	13·04	1·2966	−4667 „	−4669 „ 13
29. 12·622	10·98	1·3221	−4755 „	−4755 „ 11
30. 12·610	9·055	1·3413	−4828 „	−4830 „ 9
31. 12·620	6·91	1·3744	−4943 „	−4939 „ 7
32. 12·588	4·98	1·3960	−5033 „	−5033 „ 5
33. 12·503	2·99	1·4155	−5138 „	−5138 „ 3

Series with Thermometer '08 B.

	w.	*t*°.	*t*−*t*′.	M at *t*.	M at T.	Whole degrees C.
34.	12·543	24 905	1·1666	−4222 cal		−4218 cal. at 25°
35.	12·608	23 015	1·1913	−4289 ,,		−4290 ,, 23
36.	12 519	21·09	1·2059	−4372 ,,		−4374 ,, 21
37.	12·512	19·045	1·2292	−4448 ,,		−4450 ,, 19
38.	12·538	16·87	1·2519	−4532 ,,		−4527 ,, 17
39.	12·591	14·94	1·2779	−4606 ,,		−4604 ,, 15
40.	12 562	13 005	1·2954	−4680 ,,		−4680 ,, 13
41.	12·555	4·02	1·4094	−5093 ,,		−5092 ,, 4

Series with Thermometer '61 B.

	w.	*t*°.	*t*−*t*′.	M at *t*.	M at T.	Whole degrees C.
42.	12·603	25·00	1·1750	−4233 cal.		−4232 cal. at 25°
43.	12·564	22·94	1·1875	−4292 ,,		−4289 ,, 23
44.	12·604	20·975	1·2112	−4374 ,,		−4374 ,, 21
45.	12·576	18 955	1·2317	−4447 ,,		−4451 ,, 19
46.	12 620	16·883	1·2586	−4528 ,,		−4522 ,, 17
47.	12 596	14 96	1·2762	−4599 ,,		−4596 ,, 15
48.	12·582	13 01	1·2978	−4682 ,,		−4681 ,, 13

TABLE B.—*Heat of Dissolution of Sodium Chloride.* NaCl = 58 365; $\frac{1}{6}$ *mol.* = 9·727 *grams.*

Series with Thermometer '08 A.

	w.	*t*°.	*t*−*t*′.	M at *t*.	M at T.	Whole degrees C.
1.	9·935	24·96	0·2847	−1029 cal.		−1028 cal. at 25°
2.	9 906	23·905	0·2965	−1066 ,,	−1065	−1050 ,, 24
3.	9·785	23 885	0·2848	−1037 ,,	−1035	
4.	9 922	22·84	0 3004	−1078 ,,	−1076	−1082 ,, 23
5.	9·744	22·795	0·2986	−1088 ,,	−1086	
6.	9·718	21·98	0·2973	−1090 ,,	−1090	−1102 ,, 22
7.	9·806	22·035	0·3031	−1110 ,,	−1113	
8.	9·804	20 895	0·3143	−1141 ,,		−1138 ,, 21
9.	9·852	20 05	0·3241	−1172 ,,		−1174 ,, 20
10.	9·715	18 81	0·3293	−1207 ,,		−1202 ,, 19
11.	9·865	17 93	0·3445	−1243 ,,		−1239 ,, 18
12.	9 731	17·05	0·3467	−1266 ,,		−1268 ,, 17
13.	9·721	16 03	0·3560	−1304 ,,		−1304 ,, 16
14.	9·628	15·00	0 3612	−1336 ,,		−1336 ,, 15
15.	9·618	14·03	0·3696	−1368 ,,		−1369 ,, 14
16.	9·534	13 43	0·3671	−1371 ,,		
17.	9·872	12·01	0·3916	−1411 ,,		−1411 ,, 12
18.	9·794	10·01	0·4074	−1481 ,,		−1481 ,, 10
19.	9·979	7 995	0·4345	−1550 ,,		−1550 ,, 8
20.	9·874	5·97	0·4574	−1649 ,,		−1649 ,, 6
21.	9·857	3·925	0·4831	−1739 ,,		−1736 ,, 4
22.	9·839	3 08	0·4893	−1770 ,,		−1774 ,, 3

	w.	*t*°.	(*t*−*t*′)°.	M at *t*.	M at T. Whole degrees C.
Series with Thermometer '61 A.					
23.	9·934	24·93	0·2817	−1024 cal.	−1020 cal. at 25°
24.	9·850	23·89	0·2873	−1039 ,,	−1037 ,, 24
25.	9·928	22·955	0·2998	−1075 ,,	−1073 ,, 23
26.	9·842	21·90	0·3053	−1105 ,,	−1102 ,, 22
27.	9·907	20·905	0·3148	−1132 ,,	−1130 ,, 21
28.	9·841	19·995	0·3208	−1161 ,,	−1162 ,, 20
29.	10·828	18·955	0·3616	−1189 ,,	−1188 ,, 19
30.	9·900	16·905	0·3486	−1254 ,,	−1252 ,, 17
31.	9·860	15·005	0·3154	−1320 ,,	−1320 ,, 15
32	9·850	13·03	0·3823	−1382 ,,	−1382 ,, 13
33.	9·909	10·985	0·4025	−1446 ,,	−1444 ,, 11
34.	10·000	9·035	0·4282	−1525 ,,	−1527 ,, 9
35.	9·899	6·905	0·4116	−1599 ,,	−1595 ,, 7
36.	9·923	4·98	0·4723	−1695 ,,	−1695 ,, 5
37.	9·779	2·99	0·4876	−1775 ,,	−1775 ,, 3
Series with Thermometer '08 B.					
38.	9·913	21·905	0·2844	−1022 cal.	−1021 cal. at 25°
39.	9·930	23·01	0·2974	−1071 ,,	−1072 ,, 23
40.	9·814	21·09	0·3134	−1137 ,,	−1138 ,, 21
41.	9·796	19·045	0·3259	−1185 ,,	−1190 ,, 19
42.	9·867	16·865	0·3481	−1259 ,,	−1254 ,, 17
43.	9·812	14·94	0·3698	−1342 ,,	−1336 ,, 15
44.	9·831	13·005	0·3838	−1390 ,,	−1390 ,, 13
45.	9·837	4·02	0·4785	−1731 ,,	−1732 ,, 4
Series with Thermometer '61 B.					
46.	9·845	25·00	0·2833	−1025 cal.	−1025 cal. at 25°
47.	9·946	22·945	0·2974	−1075 ,,	−1071 ,, 23
48.	9·880	20·97	0·3153	−1136 ,,	−1134 ,, 21
49.	9·746	18·965	0·3267	−1194 ,,	−1192 ,, 19
50.	9·982	16·88	0·3516	−1254 ,,	−1241 ,, 17
51.	9·889	14·955	0·3664	−1319 ,,	−1315 ,, 15
52.	9·806	13·01	0·3804	−1381 ,,	−1382 ,, 13

TABLE C.—*Heat of Dissolution of Potassium Nitrate.* $KNO_3 = 100·92$; $\frac{1}{6}$ *mol.* = 16·82 *grams.*

w.	*t*°.	(*t*−*t*′)°.	M at *t*.	M at T.	Whole degrees C.
		Series with Thermometer '08 A.			
1. 16·942	24·95	2·2622	−8223 cal		−8220 cal. at 25°
2. 16·886	23·905	2·2673	−8268 „		−8262 „ 24
3. 17·015	22·85	2·2886	−8282 „		−8281 „ 23
4. 16·906	21·985	2·2803	−8305 „		−8305 „ 22
5. 16·871	20·895	2·2819	−8339 „		−8336 „ 21
6. 16·882	20·05	2·2946	−8369 „		−8372 „ 20
7. 16·853	18·805	2·3016	−8420 „		−8412 „ 19
8. 16·885	17·94	2·3156	−8413 „	− 8142	−8452 „ 18
9. 16·688	17·91	2·2912	−8464 „	− 8461	
10. 16·605	17·06	2·2915	−8496 „	−(8497)	−8488 „ 17
11. 16·792	16·91	2·3149	−8487 „	− 8483	
12. 16·635	16·025	2·2965	−8500 „		−8502 „ 16
13. 16·927	15·02	2·3474	−8542 „	− 8543	−8546 „ 15
14. 16·926	14·98	2·3501	−8549 „	− 8548	
15. 16·890	14·03	2·3555	−8587 „	− 8590	−8580 „ 14
16. 18·715	13·92	2·6061	−8574 „	− 8579	
17. 16·913	13·535	2·3654	−8590 „		
18. 16·777	13·515	2·3419	−8593 „		
19. 16·936	12·01	2·3838	−8666 „		−8666 „ 12
20. 16·400	10·09	2·3305	−8749 „		−8754 „ 10
21. 16·917	8·00	2·4249	−8823 „		−8823 „ 8
22. 16·729	5·97	2·4253	−8924 „		−8924 „ 6
23. 16·910	3·93	2·4774	−9016 „		−9013 „ 4
24. 16·774	3·08	2·4596	−9026 „		−9031 „ 3
		Series with Thermometer '61 A.			
25. 15·522	23·88	2·2602	−8264 cal.		−8256 cal. at 24°
26. 16·886	22·96	2·2786	−8307 „		−8306 „ 23
27. 16·910	21·90	2·2897	−8339 „		−8335 „ 22
28. 16·909	19·95	2·2891	−8374 „	− 8372	−8381 „ 20
29. 16·825	19·775	2·2946	−8399 „	− 8390	
30. 16·758	18·955	2·2933	−8428 „		−8425 „ 19
31. 16·834	18·005	2·3131	−8462 „	− 8462	−8465 „ 18
32. 16·683	17·92	2·2921	−8464 „	− 8459	
33. 16·764	17·86	2·3075	−8479 „	− 8473	
34. 16·851	16·93	2·3226	−8488 „		−8484 „ 17
35. 16·914	15·935	2·3421	−8527 „		−8524 „ 16
36. 16·885	15·005	2·3451	−8554 „		−8554 „ 15
37. 16·938	13·99	2·3665	−8604 „		−8604 „ 14
38. 16·937	12·925	2·3610	−8585 „	− 8581	−8606 „ 13
39. 16·949	13·05	2·3752	−8629 „	− 8630	
40. 16·867	10·98	2·3613	−8681 „		−8681 „ 11
41. 16·889	9·05	2·4035	−8762 „		−8764 „ 9
42. 16·858	6·92	2·4277	−8866 „		−8862 „ 7
43. 16·909	4·97	2·4586	−8958 „		−8953 „ 5
44. 16·810	2·99	2·4666	−9035 „		−9035 „ 3

TABLE D.—*Heat of Dissolution of Anhydrous Strontium Chloride,*

$SrCl_2 = 158{\cdot}04$; $\frac{1}{12}$ *mol.* = 13·17 *grams.*

w.	*t°.*	*(t′−t)°.*	M at *t°.*	M. at T. Whole degrees C.
		Series with Thermometer '08 A.		
1. 13·125	24·84	1·6095	11826 cal.	11832 cal. at 25°
2. 13·198	23·78	1·6099	11771 ,,	11782 ,, 24
3. 13·215	22·72	1·6043	11706 ,,	11724 ,, 23
4. 13·181	21·855	1·5878	11615 ,,	11633 ,, 22
5. 13·231	20·765	1·5835	11540 ,,	11562 } 11554 ,, 21
6. 13·186	20·635	1·5743	11515 ,,	11547
7. 13·255	19·93	1·5753	11459 ,,	11463 ,, 20
8. 13·312	18·69	1·5704	11375 ,,	11398 ,, 19
9. 13·210	17·80	1·5495	11309 ,,	11325 ,, 18
10. 13·250	16·845	1·5385	11195 ,,	11214 ,, 17
11. 13·274	15·82	1·5312	11122 ,,	11132 ,, 16
12. 13·275	14·815	1·5234	11065 ,,	11073 ,, 15
13. 13·321	13·74	1·5160	10973 ,,	10992 ,, 14
14. 13·143	11·87	1·4676	10756 ,,	10773 ,, 12
15. 13 163	9·93	1·4469	10596 ,,	10600 ,, 10
16. 13·208	7·86	1·4246	10396 ,,	10412 ,, 8
17. 13·174	3·805	1·3515	9888 ,,	9912 ,, 4
18. 13·176	2·945	1·3360	9817 ,,	9822 ,, 3
		Series with Thermometer '61 A.		
19. 13·178	23·64	1·6087	11788 cal.	11800 cal. at 24°
20. 13·215	22·715	1·6009	11685 ,,	11717 ,, 23
21. 13·201	21·65	1·5911	11632 ,,	11650 ,, 22
22 13·237	19·74	1·5658	11414 ,,	11410 20
23. 13·210	18·71	1·5486	11306 ,,	11321 19
24. 13·227	17·745	1·5410	11236 ,,	11250 18
25. 13·252	16·685	1·5337	11162 ,,	11185 17
26. 13·267	15·67	1·5319	11135 ,,	11146 16
27. 13·232	14·80	1·5177	11062 ,,	11080 15
28. 13·139	13·775	1·4982	10997 ,,	11018 14
29. 13 234	12·805	1·4937	10885 ,,	10908 13
30. 13·168	10·765	1·4584	10655 ,,	10683 11
31. 13·150	8·845	1·4282	10482 ,,	10483 9
32. 13·153	6·73	1·4012	10271 ,,	10294 7
33. 13·219	3·76	1·3596	9915 ,,	9928 4
34. 13·215	2·81	1·3517	9862 ,,	9880 3
		Series with Thermometer '08 B.		
35. 13·196	24·90	1·6182	11825 cal.	11830 cal. at 25°
36. 13·222	23·01	1·6020	11693 ,,	11682 ,, 23
37. 13·123	21·09	1·5694	11531 ,,	11523 ,, 21
38. 13·175	19·045	1·5522	11364 ,,	11360 ,, 19
39. 13·161	16·875	1·5245	11168 ,,	11180 ,, 17
40. 13·196	14·945	1·5061	11003 ,,	11007 ,, 15
41. 13·146	14·045	1·4916	10938 ,,	10933 ,, 14
42. 13·215	12·955	1·4849	10832 ,,	10836 ,, 13

w.	t°.	(t′−t)°.	M at t°.	M. at T. Whole degrees C.
		Series with Thermometer '61 B.		
43. 13·213	25·00	1·6149	11789 cal.	11789 cal. at 25°
44. 13·206	22·94	1·5961	11657 „	11658 „ 23
45. 13·188	20·975	1·5668	11458 „	11458 „ 21
46. 13·205	18·955	1·5495	11317 „	11318 „ 19
47. 13·208	16·88	1·5290	11163 „	11176 „ 17
48. 13·208	14·965	1·5070	11003 „	11007 „ 15

TABLE E.—*Heat of Dissolution of Hydrated Strontium Chloride,*

$SrCl_2,5{\cdot}992H_2O = 265{\cdot}66;\ \frac{1}{12}\ mol. = 22{\cdot}138\ grams.$

w.	t°.	(t−t′)°.	m at t°.		m at T. Whole degrees C.	M at T.
		Series with Thermometer '08 A.				
1. 22·255	24·96	0·9866	−7292 cal.		−7291 cal. at 25°	2534 cal.
2. 22·145	23·91	0·9872	−7332 „		−7326 „ 21	2449 „
3. 22·125	22·85	0·9912	−7370 „		−7364 „ 23	2361 „
4. 22·192	21·98	0·9970	−7393 „		−7393 „ 22	2283 „
5. 22·086	20·855	0·9968	−7423 „		−7421 „ 21	2204 „
6. 22·308	20·05	1·0141	−7482 „		−7484 „ 20	2090 „
7. 23·384	18·815	1·0692	−7525 „		−7522 „ 19	1999 „
8. 22·264	17·935	1·0201	−7536 „		−7534 „ 18	1938 „
9. 22·237	17·05	1·0258	−7588 „		−7590 „ 17	1828 „
10. 21·776	16·01	1·0128	−7648 „		−7648 „ 16	1718 „
11. 21·940	15·015	1·0214	−7656 „	−7656	−7645 „ 15	1670 „
12. 22·210	14·98	1·0310	−7634 „	−7634		
13. 22·187	14·02	1·0104	−7713 „		−7713 „ 14	1551 „
15. 22·155	13·475	1·0413	−7730 „			
14. 22·257	12·01	1·0509	−7777 „		−7777 „ 12	1382 „
16. 22·243	10·005	1·0629	−7758 „		−7758 „ 10	1298 „
17. 22·238	8·00	1·0700	−7911 „		−7911 „ 8	1040 „
18. 22·238	4·935	1·0985	−8122 „		−8119 „ 5	675 „
19. 22·232	3·93	1·1055	−8177 „		−8173 „ 4	570 „
20. 22·262	3·085	1·1115	−8209 „		−8204 „ 3	485 „
		Series with Thermometer '61 A.				
21. 22·262	24·925	0·9886	−7306 cal.		−7304 cal. at 25°	2521 cal.
22. 22·188	23·885	0·9881	−7329 „		−7324 „ 21	2451 „
23. 22·247	22·95	0·9975	−7377 „		−7374 „ 23	2351 „
24. 22·220	21·90	1·0033	−7429 „		−7422 „ 22	2254 „
25. 22·247	20·895	1·0049	−7431 „		−7430 „ 21	2195 „
26. 22·216	19·99	1·0096	−7474 „		−7474 „ 20	2100 „
27. 22·178	18·96	1·0121	−7506 „		−7504 „ 19	2014 „
28. 22·238	17·92	1·3128	−7567 „		−7561 „ 18	1911 „
29. 22·243	16·905	1·0258	−7586 „		−7583 „ 17	1935 „
30. 22·192	15·93	1·0261	−7605 „		−7601 „ 16	1765 „
31. 22·228	14·83	1·0338	−7652 „		−7645 „ 15	1670 „
32. 22·252	13·98	1·0404	−7697 „		−7696 „ 14	1568 „
33. 22·310	13·05	1·0481	−7727 „		−7729 „ 13	1483 „
34. 22·263	10·98	1·0567	−7807 „		−7807 „ 11	1300 „
35. 22·228	9·05	1·0664	−7890 „		−7894 „ 9	1110 „
36. 22·236	6·905	1·0856	−8080 „		−8023 „ 7	875 „
37. 22·210	4·98	1·0932	−8095 „	−8095	−8099 „ 5	746 „
38. 22·249	4·905	1·0964	−8106 „	−8102		
39. 22·225	2·99	1·1111	−8221 „		−8221 „ 3	468 „

TABLE F.—*Heat of Dissolution of Anhydrous Strontium Nitrate.*

$Sr(NO_3)_2 = 211{\cdot}08$; $\frac{1}{12}$ *mol.* = 17·59 *grams.*

w.	t°.	(t − t′)°.	M at t.	M at T. Whole degrees C.	
Series with Thermometer '08 A.					
1. 17·808	24·96	0·6023	−4356 cal.		−4355 cal. at 25°
2. 17·841	23·91	0·6116	−4415 ,,		−4408 ,, 24
3. 17·946	22·85	0·6216	−4461 ,,		−4460 ,, 23
4. 17·810	21·98	0·6262	−4528 ,,		−4528 ,, 22
5. 17·801	20·95	0·6350	−4594 ,,		−4587 ,, 21
6. 17·682	20·05	0·6390	−4654 ,,		−4657 ,, 20
7. 17·631	18·81	0·6477	−4731 ,,		−4720 ,, 19
8. 17·698	18·00	0·7108	−4760 ,,	−4760 }	−4762 ,, 18
9. 18·751	17·94	0·6964	−4767 ,,	−4764 }	
10. 17·808	17·07	0·6742	−4875 ,,		−4880 ,, 17
11. 17·725	16·00	0·6822	−4957 ,,		−4957 ,, 16
12. 17·641	15·015	0·6829	−4986 ,,		−4986 ,, 15
13. 17·487	14·03	0·6928	−5102 ,,		−5103 ,, 14
14. 17·487	13·43	0·6946	−5114 ,,		
15. 17·764	12·01	0·7174	−5195 ,,		−5195 ,, 12
16. 17·723	10·01	0·7248	−5351 ,,		−5351 ,, 10
17. 17·758	7 995	0·7582	−5496 ,,		−5196 ,, 8
18. 17·693	4·935	0·7948	−5783 ,,		−5776 ,, 5
19. 17·776	3·925	0·8132	−5889 ,,		−5880 ,, 4
20. 17·748	3·08	0·8195	−5943 ,,		−5947 ,, 3
Series with Thermometer '61 A.					
21. 17·784	24·595	0·6019	−4360 cal.		−4340 cal. at 25°
22. 17·880	23·89	0·6099	−4390 ,,		−4385 ,, 24
23 17·888	22·955	0·6204	−4466 ,,		−4463 ,, 23
24. 17·899	21·90	0.6274	−4513 ,,		−4506 ,, 22
25. 17·859	19·985	0·6424	−4632 ,,		−4632 ,, 20
26. 17·882	18·95	0·6555	−4720 ,,		−4715 ,, 19
27. 17·905	18·005	0·6652	−4784 ,,		−4784 ,, 18
28. 17·869	16·905	0·6730	−4851 ,,		−4844 ,, 17
29. 17·840	15·935	0·6791	−4904 ,,		−4900 ,, 16
30. 17·803	15·03	0·6878	−4976 ,,		−4978 ,, 15
31. 17·892	13·975	0·7027	−5058 ,,		−5056 ,, 14
32. 17·864	13·035	0 7058	−5120 ,,		−5122 ,, 13
33. 17·736	10·98	0·7253	−5267 ,,		−5267 ,, 11
34. 17·881	9·05	0·7537	−5428 ,,		−5432 ,, 9
35. 17·820	6 94	0·7736	−5590 ,,		−5586 ,, 7
36. 17·763	4·91	0·7989	−5791 ,,		−5785 ,, 5
37. 17·782	3·96	0·8125	−5883 ,,		−5879 ,, 4
38. 17·791	2·995	0·8247	−5955 ,,		−5955 ,, 3
Series with Thermometer '08 A.					
39. 17·744	20·955	0·6360	−4616 cal.		−4610 cal. at 21°
40. 17·733	20·01	0·6418	−4661 ,,		−4662 ,, 20
41. 17·718	18·98	0·6519	−4738 ,,		−4737 ,, 19
42. 17·681	17·92	0·6617	−4815 ,,		−4808 ,, 18
43. 17·839	16·98	0·6733	−4860 ,,		−4860 ,, 17
44. 17·699	16·00	0·6790	−4940 ,,		−4940 ,, 16
45. 17·683	4·04	0·8049	−5860 ,,		−5863 ,, 4

Series with Thermometer '61 A.

	w.	*t*°.	(*t*−*t*)°.	M at *t*°.	M at T.	Whole degrees C.
46.	17·750	20·88	0·6345	−4605 cal.	−4597 cal. at	21°
47.	17·791	19·96	0·6449	−4673	−4670	20
48.	17·724	19·06	0·6498	−4723	−4726	19
49.	17·862	17·925	0·6612	−4768	−4763	18
50.	17·710	16·935	0·6680	−4858	−4854	17
51.	17·733	16·04	0·6761	−4911	−4912	16

TABLE G.—*Heat of Dissolution of Hydrated Strontium Nitrate.*

$Sr(NO_3)_2,3·987H_2O = 282·846; \frac{1}{12}$ *mol.* = 23·571 *grams.*

	w.	*t*°.	(*t*−*t'*)°.	*m* at *t*°.	*m* at T.	Whole degrees C.	M at T°.
				Series with Thermometer '08 A.			
1.	23·317	24·96	1·6766	-12531 cal.	−12525 cal. at	25°	−5981 cal.
2.	23 617	23·92	1·7046	-12579 „	−12575	„ 24	−6073 „
3.	23·405	22·85	1·6936	-12610 „	−12603	„ 23	−6135 „
4.	23·510	21·985	1·7038	-12630 „	−12630	„ 22	−6194 „
5.	23·635	20·89	1·7162	-12654	−12651	„ 21	−6249 „
6.	23·361	19·845	1·7028	-12701	−12694	„ 20	−6324 „
7.	23·248	18·81	1·7015	-12753	−12743	„ 19	−6409 „
8.	23·706	17·945	1·7381	-12775	−12773	„ 18	−6471 „
9.	23·742	17·06	1·7478	-12828	−12830	„ 17	−6563 „
10.	23·487	16·045	1·7329	-12857	−12859	„ 16	−6626 „
11.	23·366	15·03	1·7288	-12893	−12894	„ 15	−6696
12.	23·609	14·03	1·7520	-12932	−12933	„ 14	−6770
13.	23·652	12·01	1·7668	-13014	−13014	„ 12	−6921
14.	23·763	10·005	1·7880	-13110	−13110	„ 10	−7086
15.	23·735	8·00	1·7953	-13178	−13178	„ 8	−7224
16.	23·872	3·93	1·8416	-13439	−13436	„ 4	−7621
17.	23·792	3·08	1·8462	-13517	−13521	„ 3	−7740
				With Thermometer '08 B.			
18.	23·718	4·31	1·8339	−13470 cal.	(−13490) cal. at	4	−7675 cal.
				Series with Thermometer '61 A.			
19.	23·441	24·935	1·6926	−12588 cal.	−12585 −12559	} −12572 cal. at 25°	−6028 cal.
20.	23·473	24·915	1·6952	−12562 „			
21.	23·441	22·95	1·6983	−12628 „	−12626	„ 23	−6158 „
22.	23·740	20·905	1·7284	−12691 „	−12686	„ 21	−6284 „
23.	23·610	18·96	1·7312	−12781 „	−12779	„ 19	−6445 „
24.	23·841	17·995	1·7518	−12809 „	−12809	„ 18	−6507 „
25.	23·654	16·905	1·7410	−12835 „	−12838	„ 17	−6566 „
26.	23 519	15·915	1·7356	−12861 „	−12860	„ 16	−6627 „
27.	23·582	15·02	1·7447	−12896 „	−12897	„ 15	−6699 „
28.	23·830	13·985	1·7724	−12965 „	−12964	„ 14	−6801 „
29.	23·748	13·04	1·7725	−13011 „	−13018	„ 13	−6885 „
30.	23·763	10·98	1·7779	−13040 „	−13040	„ 11	−6982 „
31.	23·702	9·05	1·7902	−13162 „	−13164	„ 9	−7176 „
32.	23·716	6·91	1·8088	−13283 „	−13277	„ 7	−7358 „
33.	23·887	4·985	1·8350	−13387 „	−13387	„ 5	−7538 „
34.	23·820	2·99	1·8456	−13500 „	−13500	„ 3	−7719 „

TABLE H.—*Heat of Dissolution of Anhydrous Sodium Carbonate.*

$Na_2CO_3 = 105{\cdot}84$; $\frac{1}{12}$ *mol.* = 8·82 *grams.*

	w.	*t*°.	(*t'*−*t*)°.	M at *t*°.	M at T. Whole degrees C.
			Series with Thermometer '61 A.		
1.	8·825	24·605	0·7980	5839 cal.	5852 cal. at 25°
2.	8·825	24·600	0·7957	5822 ,,	
3.	8·826	21·775	0·7787	5695 ,,	5695 ,, 22
4.	8·854	21·775	0·7784	5675 ,,	
5—12.	See Trans., 1887, 73.	18·815	—	5521 ,,	5533 ,, 19
13.	8·838	15·80	0·7246	5292 ,,	5316 ,, 16
14.	8·829	15·80	0·7275	5317 ,,	
15.	8·867	12·85	0·6969	5072 ,,	5084 ,, 13
16.	8·796	12·855	0·6926	5081 ,,	
17.	8·887	12·86	0·6987	5074 ,,	
18.	8·871	9·955	0·6760	4917 ,,	4912 ,, 10
19.	8·778	9·95	0·6674	4906 ,,	
20.	8·819	6·925	0·6420	4697 ,,	4701 ,, 70
21.	8·763	6·93	0·6382	4699 ,,	
22.	8·740	3·94	0·5811	4290 ,,	4315 ,, 4
23.	8·743	3·935	0·5864	4327 ,,	

TABLE I.—*Heat of Dissolution of Hydrated Sodium Carbonate.*

$Na_2CO_3,9{\cdot}96H_2O = 284{\cdot}722$; $\frac{1}{12}$ *mol.* = 23·719 *grams.*

	w.	*t*°.	(*t*−*t'*)°.	*m* at *t*°.	*m* at T. Whole degrees C.		M at T°.
			Series with Thermometer '08 A.				
1.	23·766	24·95	2·1745	−16285 cal.		−16286 cal. at 25°	+ 44 cal.
2.	23·870	23·905	2·1802	−16258 ,,		−16262 ,, 24	− 15 ,,
3.	23·597	22·845	2·1476	−16202 ,,		−16211 ,, 23	− 47 ,,
4.	23·488	21·985	2·1394	−16211 ,,		−16207 ,, 22	− 127 ,,
5.	23·754	20·90	2·1604	−16186 ,,		−16189 ,, 21	− 196 ,,
6.	23·955	20·05	2·1782	−16184 ,,		−16184 ,, 20	− 274 ,,
7.	23·695	18·785	2·1525	−16165 ,,		−16168 ,, 19	− 343 ,,
8.	23·891	17·94	2·1708	−16172 ,,		−16169 ,, 18	− 432 ,,
9.	23·551	17·06	2·1441	−16204 ,,		−16201 ,, 17	− 549 ,,
10.	23·636	16·025	2·1422	−16127 ,,		−16127 ,, 16	− 559 ,,
11.	23·768	15·02	2·1549	−16135 ,,		−16136 ,, 15	− 656 ,,
12.	23·677	14·02	2·1490	−16149 ,,		−16149 ,, 14	− 756 ,,
13.	23·966	13·41	2·1735	−16140 ,,	−16147	−16166 ,, 13	− 856 ,,
14.	23·877	12·93	2·1719	−16189 ,,	−16186		
15.	23·871	12·015	2·1742	−16210 ,,	−16210	−16195 ,, 12	− 972 ,,
16.	24·019	12·04	2·1833	−16179 ,,	−16179		
17.	23·856	10·01	2·1673	−16168 ,,		−16169 ,, 10	−1121 ,,
18.	24·000	8·00	2·1784	−16195 ,,		−16195 ,, 8	−1278 ,,
19.	24·012	5·965	2·1853	−16204 ,,		−16204 ,, 6	−1504 ,,
20.	24·059	3·93	2·1982	−16261 ,,		−16260 ,, 4	−1736 ,,
21.	23·756	3·08	2·1656	−16218 ,,		(−16218) ,, 3	−1781 ,,

	w.	*t*°.	(*t*−*t*′)°.	*m* at *t*°.	*m* at T.	Whole degrees C.	M at T°.
				Series with Thermometer '61 A.			
22.	23·766	24·93	2·1882	−16329 cal.		−16332 cal. at 25°	− 2 cal.
23.	23·833	23·895	2·1808	−16296 ,,		−16298 ,, 24	− 51 ,,
24.	23·817	22·965	2·1763	−16270 ,,		−16269 ,, 23	− 105 ,,
25.	23·536	21·90	2·1516	−16277 ,,		−16276 ,, 22	− 196 ,,
26.	23·393	20·905	2·1342	−16235 ,,		−16239 ,, 21	− 246 ,,
27.	23·642	19·82	2·1606	−16274 ,,	−16277	−16217 ,, 20	− 307 ,,
28.	23·701	19·95	2·1508	−16157 ,,	−16158		
29.	23·759	18·955	2·1569	−16159 ,,		−16159 ,, 19	− 334 ,,
30.	23·727	18·005	2·1507	−16134 ,,		−16134 ,, 18	− 309 ,,
31.	23·524	16·905	2·1397	−16186 ,,		−16182 ,, 17	− 415 ,,
32.	23·485	15·93	2·1319	−16153 ,,		−16153 ,, 16	− 587 ,,
33.	23·788	15·005	2·1572	−16143 ,,		−16143 ,, 15	− 663 ,,
34.	23·453	13·985	2·1384	−16225 ,,	(−16225)	−16178 ,, 14	− 785 ,,
35.	23·474	13·99	2·1304	−16154 ,,	−16154		
36.	23·562	13·03	2·1413	−16179 ,,		−16179 ,, 13	− 869 ,,
37.	23·060	10·97	2·1845	−16167 ,,		−16167 ,, 11	−1032 ,,
38.	23·952	9·05	2·1759	−16171 ,,		−16172 ,, 9	−1207 ,,
39.	23·960	6·965	2·1777	−16179 ,,	−16180	−16196 ,, 7	−1108 ,,
40.	23·909	6·955	2·1773	−16211 ,,	−16212		
41.	23·911	4·91	2·1808	−16238 ,,		−16240 ,, 5	−1628 ,,
42.	23·891	2·985	2·1835	−16259 ,,		−16259 ,, 3	−1822 ,,
				Series with Thermometer '08 D.			
43.	23·827	24·945	2·1900	−16364 cal.		−16365 cal. at 25°	− 35 cal.
44.	23·895	19·98	2·1770	−16223 ,,		−16221 ,, 20	− 311 ,,
45.	22·827	16·98	2·1933	−16161 ,,	−16161	−16175 ,, 17	− 523 ,,
46.	23·937	16·96	2·1768	−16188 ,,	−16189		
				Series with Thermometer '61 D.			
47.	23·420	24·835	2·1458	−16313 cal.		−16317 cal. at 25°	+ 13 cal.
48.	23·866	19·96	2·1734	−16215 ,,		−16216 ,, 20	− 306 ,,
49.	23·784	17·00	2·1536	−16121 ,,	−16121	−16145 ,, 17	− 403 ,,
50.	23·769	16·93	2·1583	−16166 ,,	−16169		

TABLE J.—*Heat of Dissolution of Anhydrous Sodium Acetate.*

$NaC_2H_3O_2 = 81{\cdot}855$; $\frac{1}{6}$ *mol.* = 13·643 *grams.*

	w.	*t*°.	(*t′* − *t*)°.	M at *t*°.	M at T.	Whole degrees C.
Series with Thermometer '08 A.						
1.	13·652	24·95	1·0870	3977 cal.		3977 cal. at 25°
2.	13·676	23·915	1·0826	3972 „		3972 „ 24
3.	13·678	22·845	1·0887	3976 „		3976 „ 23
4.	13·713	21·98	1·0935	3982 „		3982 „ 22
5.	13·745	20·895	1·0941	3975 „		3975 „ 21
6.	13·784	20·05	1·0973	3984 „		3983 „ 20
7.	13·711	18·805	1·0875	3960 „		3963 „ 19
8.	13·626	17·94	1·0826	3967 „		3967 „ 18
9.	13·657	17·05	1·0748	3930 „		3930 „ 17
10.	13·735	16·06	1·0818	3933 „		3932 „ 16
11.	13·928	15·02	1·0971	3934 „		3934 „ 15
12	13·657	14·015	1·0820	3931 „		3931 „ 14
13.	13·659	13·43	1·0770	3937 „		
14.	13·629	12·93	1·0669	3908 „		3908 „ 13
15.	13·719	12·01	1·0634	3867 „	3867 3887 }	3877 „ 12
16.	13·620	11·90	1·0600	3886 „		
17.	13·627	10·005	1·0541	3162 „		3862 „ 10
18.	13·625	8·00	1·0506	3846 „	3846 3835 }	3842 „ 8
19.	13·686	7·95	1·0511	3834 „		
20.	13·670	5·97	1·0442	3813 „		3813 „ 6
21.	13·673	3·93	1·0342	3776 „		3778 „ 4
22.	13·643	3·08	1·0227	3742 „	3741 3748 }	3745 „ 3
23.	13·656	2·525	1·0219	3735 „		
Series with Thermometer '61 A.						
24.	13·705	24·93	1·0892	3970 cal.		3970 cal. at 25°
25.	13·640	23·895	1·0862	3975 „		3975 „ 24
26.	13·618	22·95	1·0866	3977 „		3977 „ 23
27.	13·648	21·89	1·0830	3964 „		3965 „ 22
28.	13·644	20·91	1·0814	3960 „		3960 „ 21
29.	13·660	19·99	1·0760	3935 „		3935 „ 20
30.	13·639	18·95	1·0734	3932 „		3932 „ 19
31.	13·689	18·00	1·0797	3940 „		3940 „ 18
32.	13·601	16·90	1·0709	3934 „		3934 „ 17
33.	13·640	15·93	1·0757	3939 „		3939 „ 16
34.	13·618	15·04	1·0726	3930 „		3930 15
35.	13·716	13·98	1 0777	3925 „		3925 14
36.	13·675	13·04	1·0674	3902 „		3902 13
37.	13·666	11·925	1·0612	3878 „		3879 12
38.	13·665	10·98	1·0552	3856 „		3856 11
39.	13·688	9·05	1·0568	3856 „		3856 „ 9
40.	13·610	7·935	1·0452	3835 „		3836 „ 8
41.	13·620	6·925	1·0413	3818 „		3820 „ 7
42.	13·698	4·98	1·0353	3774 „		3774 „ 5
43.	13·688	2·985	1·0223	3739 „		3740 „ 3

w.	*t.*	$(t-t')°$.	M at $t°$.	M at T.	Whole degrees C.
		Series with Thermometer '08 B.			
44. 13·607	24·905	1·0813	3957 cal.		3957 cal. at 25°
45. 13·619	23·01	1·0798	3960 „		3960 „ 23
46. 13·614	21·095	1·0856	3982 „		3982 „ 21
47. 13·617	19·04	1·0740	3939 „		3940 „ 19
48. 13·639	16·87	1·0754	3937 „		3938 „ 17
49. 13·606	14·94	1·0696	3925 „		3926 „ 15
50. 13·588	14·04	1·0638	3909 „		3908 „ 14
51. 13·567	12·01	1·0553	3884 „		3884 „ 12
52. 13·659	9·925	1·0574	3865 „		3865 „ 10
53. 13·597	9·03	1·0500	3855 „		3854 „ 9
54. 13·707	7·97	1·0540	3838 „		3838 „ 8
55. 13·654	5·935	1·0418	3809 „		3810 „ 6
		Series with Thermometer '61 B.			
56. 13·668	25·00	1·0885	3978 cal.		3978 cal. at 25°
57. 13·614	22·945	1·0875	3990 „		3990 „ 23
58. 13·643	20·975	1·0871	3980 „		3981 „ 21
59. 13·623	18·955	1·0790	3953 „		3956 „ 19
60. 13·652	16·885	1·0763	3938 „		3938 „ 17
61. 13·616	14·96	1·0721	3933 „		3933 „ 15
62. 13·583	13·975	1·0660	3920 „		3920 „ 14
63. 13·655	11·975	1·0673	3903 „		3904 „ 12
64. 13·584	9·96	1·0532	3872 „		3973 „ 10
65. 13·692	9·04	1·0581	3859 „		3856 „ 9
66. 13·670	7·97	1·0526	3845 „		3845 „ 8
67. 13·647	5·915	1·0418	3812 „		3814 „ 6
		Series with Thermometer '61 C.			
68. 13·703	23·955	1·0920	3983 cal.	3983 3977 }	3980 cal. at 24°
69. 13·666	23·98	1·0875	3977 „		
70. 13·670	21·93	1·0902	3984 „		3984 „ 22
71. 13·638	20·1	1·0817	3961 „		3960 „ 20
72. 13·663	18·075	1·0811	3952 „		3951 „ 19
73. 13·643	17·00	1·0793	3951 „	3951 3950 }	3950 „ 17
74. 13·639	17·01	1·0787	3950 „		
75. 13·625	15·10	1·0728	3938 „		3933 „ 15
76. 13·582	14·065	1·0648	3915 „		3914 „ 14
77. 13·599	12·90	1·0636	3905 „		3906 „ 13
78. 13 626	11·93	1·0626	3895 „		3895 „ 12
79. 13·648	10·93	1·0574	3878 „		3879 „ 11
80. 13·669	9·06	1·0532	3848 „		3848 „ 9
81. 13·610	8·07	1·0464	3839 „		3838 „ 8
82. 13·621	6·08	1·0429	3823 „		3822 „ 6

TABLE K.—*Heat of Dissolution of Hydrated Sodium Acetate,* $NaC_2H_3O_2,3H_2O = 135{\cdot}755$; $\frac{1}{6}$ *mol.* = 22·625 *grams.*

	w.	*t*°.	(*t*−*t*′)°.	*m* at *t*°.	*m* at T.	Whole degrees C.	M. at T.°
				Series with Thermometer '08 A.			
1.	22·458	24·96	1·3100	−4902 cal.		−4903 cal. at 25°	+ 7 cal.
2.	22·481	23·92	1·3044	−4876 „		−4878 „ 24	+ 18 „
3.	22·547	22·85	1·3038	−4860 „		−4862 „ 23	+ 8 „
4.	22·701	21·975	1·3083	−4844 „		−4845 „ 22	+ 0 „
5.	22·611	20·895	1·2919	−4802 „		−4805 „ 21	+ 13 „
6.	22·460	20·045	1·2818	−4796 „		−4796 „ 20	
7.	22·506	18·82	1·2792	−4776 „		−4779 „ 19	− 16 „
8.	22·791	18·01	1·2918	−4765 „	−4765 }	−4760 „ 18	− 13 „
9.	22·545	17 935	1·2752	−4753 „	−4754 }		
10.	22·606	17·07	1·2818	−4765 „		−4764 „ 17	− 49 „
11.	22·425	16·02	1·2651	−4740 „		−4740 „ 16	− 50 „
12.	22·736	15·05	1·2781	−4725 „		−4726 „ 15	− 61 „
13.	22·440	14·02	1·2612	−4723 „		−4723 „ 14	− 85 „
14.	22·320	13·43	1·2486	−4700 „			
15.	22·773	12·01	1·2657	−4671 „		−4671 „ 12	− 85 „
16.	22·595	10·01	1·2495	−4647 „		−4647 „ 10	−108 „
17.	22·722	8·00	1·2455	−4606 „		−4606 „ 8	−122 „
18.	22·836	3·93	1·2498	−4598 „		−4598 „ 4	−220 „
19.	22·724	3·08	1·2448	−4602 „		−4602 „ 3	−252 „
				Series with Thermometer '61 A.			
20.	22·708	23·895	1·3183	−4875 cal.		−4875 cal. at 24°	+ 21 cal.
21.	22·670	22·95	1·3144	−4875 „		−4876 „ 23	− 6 „
22.	22·558	21·89	1·3016	−4850 „		−4854 „ 22	− 9 „
23.	22·716	20·905	1·3061	−4833 „		−4836 „ 21	− 18 „
24.	22·726	19·99	1·2999	−4808 „		−4809 „ 20	− 13 „
25.	22·732	18·955	1·2706	−4798 „		−4799 „ 19	− 36 „
26.	22·770	18·01	1·2933	−4774 „	−4774 }	−4772 „ 18	− 31 „
27.	22·558	17·915	1·2792	−4768 „	−4770 }		
28.	22·655	16·905	1·2818	−4756 „			
29.	22·668	15·915	1·2773	−4736 „		−4736 „ 16	− 46 „
30.	22·497	15·00	1·2656	−4728 „		−4728 „ 15	− 63 „
31.	22·804	13·975	1·2792	−4716 „		−4717 „ 14	− 79 „
32.	22·607	13·035	1·2626	−4694 „		−4694 „ 13	− 81 „
33.	22·813	10·98	1·2647	−4661 „		−4661 „ 11	− 99 „
34.	22·793	9·045	1·2575	−4637 „		−4036 „ 19	−126 „
35.	22·673	6·91	1·2415	−4602 „		−4604 „ 7	−147 „
36.	22·771	4·985	1·2501	−4614 „		−4615 „ 5	−212 „
37.	22·766	3·965	1·2477	−4606 „		−4606 „ 4	−228 „
38.	22·650	2·99	1·2436	−4598 „		−4598 „ 3	−248 „

TABLE L.—*Heat of Dissolution of Anhydrous Rochelle Salt.*

$KNaC_4H_4O_6 = 209·665$; $\frac{1}{12}$ *mol.* = 17·472 *grams.*

w.	t°.	(t′−t)°.	M at t°.	M at T. Whole degrees C.
		Series with Thermometer '08 A.		
1. 17·457	20·935	0·3657	−2677 cal.	−2676 cal. at 21°
2. 17·447	20·03	0·3438	−2686 ,,	−2688 ,, 20
3. 17·452	17·965	0·3868	−2834 ,,	−2831 ,, 18
4. 17·469	16·885	0·3720	−2871 ,,	−2868 ,, 17
5. 17·443	16·005	0·3960	−2903 ,,	−2903 ,, 16
6. 17·496	12·01	0·4302	−3144 ,,	−3144 ,, 12
7. 17·528	10·01	0·4495	−3278 ,,	−3278 ,, 10
8. 17·479	7·995	0·4651	−3401 ,,	−3401 ,, 8
9. 17·474	6·96	0·4834	−3536 ,,	−3530 ,, 7
10. 17·469	5·97	0·4919	−3599 ,,	−3598 ,, 6
11. 17·445	3·93	0·5198	−3808 ,,	−3702 ,, 4
12. 17·455	3·085	0·5207	−3813 ,,	−3817 ,, 3
		Series with Thermometer '61 A.		
13. 17·499	24·925	0·3397	−2484 cal.	−2480 cal. at 25°
14. 17·466	23·895	0·3465	−2538 ,,	−2538 ,, 24
15. 17·515	22·95	0·3538	−2584 ,,	−2583 ,, 23
16. 17·457	21·89	0·3592	−2633 ,,	−2630 ,, 22
17. 17·414	20·895	0·3675	−2700 ,,	−2694 ,, 21
18. 17·425	19·94	0·3697	−2721 ,,	−2720 ,, 20
19. 17·475	18·955	0·3813	−2791 ,,	−2791 ,, 19
20. 17·4 3	18·005	0·3868	−2843 ,,	−2843 ,, 18
21. 17·464	16·905	0·3939	−2885 ,,	−2880 ,, 17
22. 17·555	15·905	0·4007	−2920 ,,	−2917 ,, 16
23. 17·475	15·01	0·4084	−2990 ,,	−2989 ,, 15
24. 17·524	13·99	0·4173	−3046 ,,	−3046 ,, 14
25. 17·499	13·04	0·4241	−3106 ,,	−3107 ,, 13
26. 17·436	10·98	0·4367	−3202 ,,	−3202 ,, 11
27. 17·453	9·05	0·4369	−3318 ,,	−3350 ,, 9
28. 17·446	6·93	0·4694	−3440 ,,	−3437 ,, 7
29. 17·490	4·98	0·5018	−3668 ,,	−3668 ,, 5
30. 17·502	2·99	0·5195	−3795 ,,	−3795 ,, 3
		Series with Thermometer '08 D.		
31. 17·456	21·005	0·3653	−2677 cal.	−2677 cal. at 21°
32. 17·466	20·10	0·3800	−2713 ,,	−2720 ,, 20
33. 17·440	17·96	0·3878	−2843 ,,	−2840 ,, 18
34. 17·418	16·98	0·3932	−2888 ,,	−2888 ,, 17
35. 17·435	16·00	0·4015	−2944 ,,	−2944 ,, 16
		Series with Thermometer '08 E.		
36. 17·458	20·935	0·3650	−2673 cal.	−2670 cal. at 21°
37. 17·440	19·945	0·3758	−2756 ,,	−2753 ,, 20

w.	*t.*°	$(t-t')$°.	M at t°.	M at T. Whole degrees C.
				Series with Thermometer '61 D.
38. 17·461	20·97	0·3691	−2699 cal.	−2697 cal. at 21°
39. 17·495	20·06	0·3753	−2745 ,,	−2747 ⎫ −2751 ,, 20
40. 17·418	20·05	0·3747	−2753 ,,	−2755 ⎭
41. 17·446	17·99	0·3882	−2848 ,,	−2848 ,, 18
42. 17·462	17·005	0·3952	−2897 ,,	−2897 ,, 17
43. 17·456	15·935	0·4029	−2950 ,,	−2948 ,, 16
				Series with Thermometer '61 C.
44. 17·457	20·9	0·3671	−2691 cal.	−2686 cal. at 21°
45. 17·453	19·96	0·3774	−2767 ,,	−2765 ,, 20

TABLE M.—*Heat of Dissolution of Hydrated Rochelle Salt.*

$$KNaC_4H_4O_6,4H_2O = 281{\cdot}505;\ \frac{1}{12}\ mol. = 23{\cdot}459\ grams.$$

w.	*t*°.	$(t-t')$°.	M at t.°	M at T. Whole degrees C.	M at T.°
				Series with Thermometer '08 A.	
1. 23·163	24·955	1·6438	−12307 cal.	−12306 cal. at 25°	−5746 cal.
2. 23·006	23·92	1·6358	−12331 ,,	−12329 ,, 24	−5801 ,,
3. 23·155	22·84	1·6470	−12335 ,,	−12334 ,, 23	−5841 ,,
4. 23·141	21·975	1·6497	−12362 ,,	−12362 ,, 22	−5903 ,,
5. 23·403	20·897	1·6673	−12355 ,,	−12353 ,, 21	−5929 ,,
6. 23·491	20·05	1·6772	−12383 ,,	−12385 ,, 20	−5995 ,,
7. 22·869	18 81	1·6399	−12453 ,,	−12427 ,, 19	−6072 ,,
8. 23·456	17·955	1·6866	−12470 ,,	−12470 ,, 18	−6149 ,,
9. 23·440	17·07	1·6909	−12510 ,,	−12511 ,, 17	−6223 ,,
10. 23·416	16·04	1·6863	−12490 ,,	−12493 ,, 16	−6289 ,,
11. 23·481	15·00	1·6938	−12510 ,,	−12510 ,, 15	−6201 ,,
12. 23·576	14·02	1·7079	−12565 ,,	−12564 ,, 14	−6380 ,,
13. 23·369	13·43	1·6959	−12584 ,,		
14. 23·603	12·01	1·7141	−12595 ,,	−12595 ,, 12	−6479 ,,
15. 23·452	10·01	1·7098	−12699 ,,	−12699 ,, 10	−6653 ,,
16. 23·522	8·00	1·7278	−12738 ,,	−12738 ,, 8	−6760 ,,
17. 23·325	5·97	1·7312	−12870 ,,	−12870 ,, 6	−6941 ,,
18. 23·488	3·93	1·7578	−12976 ,,	−12973 ,, 4	−7136 ,,
19. 23·271	3·08	1·7433	−12991 ,,	−12993 ,, 3	−7193 ,,

	w.	t°.	(t−t′)°.	M at t°.	M at T. Whole degrees C.		M at T°.
				Series with Thermometer '61 A.			
20.	23·210	24·935	1·6510	−12342 cal.		−12340 cal. at 25°	−5782 cal.
21.	23·161	23·885	1·6508	−12365 ,,		−12362 ,, 24	−5834 ,,
22.	23·348	22·965	1·6624	−12355 ,,		−12355 ,, 23	−5862 ,,
23.	23·332	21·90	1·6686	−12406 ,,		−12404 ,, 22	−5945 ,,
24.	23·361	20·91	1·6712	−12411 ,,		−12410 ,, 21	−5986 ,,
25.	23·464	19·95	1·6783	−12408 ,,		−12408 ,, 20	−6018 ,,
26.	23·502	18·96	1·6887	−12464 ,,		−12463 ,, 19	−6108 ,,
27.	23·432	18·00	1·6848	−12472 ,,		−12472 ,, 18	−6151 ,,
28.	23·430	16·905	1·6891	−12505 ,,		−12504 ,, 17	−6216 ,,
29.	23·155	15·92	1·6697	−12506 ,,		−12505 ,, 16	−6251 ,,
30.	23·373	15·005	1·6900	−12540 ,,		−12540 ,, 15	−6321 ,,
31.	23·576	13·98	1·7109	−12587 ,,		−12589 ,, 14	−6415 ,,
32.	23·455	13·035	1·7053	−12610 ,,		−12610 ,, 13	−6460 ,,
33.	23·448	10·975	1·7083	−12638 ,,		−12638 ,, 11	−6656 ,,
34.	23·440	9·05	1·7166	−12703 ,,		−12705 ,, 9	−6691 ,,
35.	23·456	6·905	1·7295	−12791 ,,		−12786 ,, 7	−6842 ,,
36.	23·483	4·98	1·7486	−12915 ,,		−12915 ,, 5	−7043 ,,
37.	23·473	2·995	1·7601	−13005 ,,		−13005 ,, 3	−7201 ,,
				Series with Thermometer '08 D.			
38.	23·573	24·945	1·6808	−12371 cal.	−12372	−12387 cal. at 25°	−5829 cal.
39.	23·365	24·94	1·6704	−12401 ,,	−12402		
40.	23·326	19 99	1·6650	−12374 ,,		−12374 ,, 20	−5984 ,,
41.	23·372	16·98	1·6882	−12510 ,,		−12510 ,, 17	−6222 ,,.
				Series with Thermometer '61 D.			
42.	23·430	24·835	1·6625	−12313 cal.		−12310 cal. at 25°	−5753 cal.
43.	23·485	21·94	1·6695	−12335 ,,		−12333 ,, 22	−5874 ,,
44.	23·355	19·86	1·6651	−12370 ,,		−12368 ,, 20	−5978 ,,
45.	23·298	17·005	1·6693	−12430 ,,	−12430	−12438 ,, 17	−6150 ,,
46.	23·502	16·93	1·6864	−12450 ,,	−12447		
				With Thermometer '61 E.			
48.	23·429	23·995	1·6674	−12350 cal.		−12350 cal. at 24°	−5822 cal.
49.							
50.	23·332	19·96	1·6680	−12403 ,,		−12402 ,, 20	−6012 ,,
51.	23·310	16·82	1·6804	−12506 ,,		−12502 ,, 17	−6214 ,,

TABLE N.—*Heat of Dissolution of Potassium Sulphate.*

$K_2SO_4 = 173{\cdot}88$; $\frac{3}{40}$ *mol.* = 13·041 *grams.*

	w.	t°.	(t−t′)°.	M at t°.	M at T. Whole degrees C.
			Series with Thermometer '08 A.		
1.	12·956	19·935	0·7799	−6398 cal.	− 6397 cal. at 20°
2.	12·998	16·88	0·8148	−6662 ,,	− 6650 ,, 17
3.	12·997	14·945	0·8348	−6826 ,,	− 6822 ,, 15
4.	13·038	13·925	0·8466	−6899 ,,	− 6898 ,, 14
5.	12·940	12·05	0·8616	−7074 ,,	− 7080 ,, 12
6.	13·003	10·09	0·8981	−7287 ,,	− 7297 ,, 10
7.	13·012	6·90	0·9324	−7618 ,,	− 7605 ,, 7
8.	13·036	3·08	0·9885	−8056 ,,	−(8063) ,, 3

	w.	*t*°.	(*t*−*t*′)°.	M at *t*°.	M at T. Whole degrees C.
			Series with Thermometer '61 B.		
9.	13·032	16·95	0·8157	−6653 cal.	−6650 cal. at 17°
10.	13·061	14·91	0·8395	−6833 „	−6823 „ 15
11.	12·977	13·94	0·8448	−6920 „	−6912 „ 14
12.	12·966	11·93	0·8657	−7096 „	−7086 „ 12
13.	13·029	9·985	0·8964	−7311 „	−7310 „ 10
14.	13·019	6·955	0·9273	−7569 „	−7554 „ 7
15.	13·009	2·99	0·9784	−7992 „	−7982 „ 3
			Series with Thermometer '61 B.		
16.	13·036	19·91	0·7866	−6415 cal.	−6405 cal. at 20°
17.	13·057	16·95	0·8191	−6684 „	−6665 „ 17
18.	13·012	14·96	0·8427	−6842 „	−6838 „ 15
19.	13·030	13·98	0·8487	−6922 „	−6922 „ 14
20.	13·076	11·97	0·8742	−7105 „	−7103 „ 12
21.	13·096	9·965	0·8995	−7299 „	−7295 „ 10
22.	13·051	7·045	0·9316	−7586 „	−7592 „ 7
23.	12·487	4·16	0·9719	−7864 „	−7877 „ 4

TABLE O.—*Heat of Dissolution of Anhydrous Magnesium Sulphate.*

$$MgSO_4 = 119{\cdot}76;\ \frac{3}{40}\ mol. = 8{\cdot}982\ grams.$$

Series with Thermometer '08 B.

1.	8·936	19·965	2·5055	20492 cal.	20496 cal. at 20°
2.	8·930	16·855	2·4803	20292 „	20304 „ 17
3.	8·918	13·395	2·4416	20000 „	20010 „ 13·5
4.	8·955	7·01	2·3857	19451 „	19451 19448 } 19450 „ 7
5.	8·979	6·965	2·3906	19444 „	
6.	8·982	3·08	2·3498	19104 „	19094 „ 3

Series with Thermometer '61 B.

7.	8·939	19·865	2·5086	20510 cal.	20512 cal. at 20°
8.	8·916	16·955	2·4821	20345 „	20349 „ 17
9.	8·918	13·45	2·4451	20034 „	20034 „ 13·5
10.	8·959	9·925	2·4172	19711 „	19716 „ 10
11.	8·955	7·04	2·3840	19450 „	19445 „ 7
12.	9·014	3·04	2·3561	19093 „	19088 „ 3

TABLE P.—*Heat of Dissolution of Hydrated Magnesium Sulphate.*

$MgSO_4,7H_2O = 245{\cdot}58$; $\frac{3}{40}$ *mol.* = 18·411 *grams.*

	w.	*t*°.	(*t*−*t'*)°.	*m* at *t*°.	*m* at T. Whole degrees C.	M at T.°
	Series with Thermometer '08 A.					
1.	18·334	19·94	0·4670	−3874 cal.	−3875 cal. at 20°	8000 cal.
2.	18·310	16·875	0·4714	−3914 ,,	−3912 ,, 17	7087 ,,
3.	18·035	14·945	0·4673	−3940 ,,	−3939 ,, 15	6945 ,,
4.	18·105	13·925	0·4736	−3958 ,,	−3957 ,, 14	6864 ,,
5.	18·263	12·05	0·4786	−3985 ,,	−3987 ,, 12	6714 ,,
6.	18·177	10·085	0·4832	−4042 ,,	−4045 ,, 10	6536 ,,
7.	18·247	6·895	0·4953	−4127 ,,	−4125 ,, 7	6276 ,,
8.	18·298	3·075	0·5138	−4269 ,,	−4272 ,, 3	5882 ,,
	Series with Thermometer '61 A.					
9.	17·997	16·96	0·4648	−3928 cal.	−3927 cal. at 17°	7072 cal.
10.	18·268	14·91	0·4787	−3961 ,,	−3960 ,, 15	6924 ,,
11.	18·091	13·94	0·4722	−3969 ,,	−3968 ,, 14	6853 ,,
12.	18·203	11·935	0·4792	−4003 ,,	−4000 ,, 12	6701 ,,
13.	20·151	9·98	0·5374	−4062 ,,	−4062 ,, 10	6519 ,,
14.	18·239	6·96	0·4948	−4125 ,,	−4124 ,, 7	6277 ,,
15.	18·257	2·99	0·5113	−4258 ,,	−4258 ,, 3	5896 ,,
	Series with Thermometer '61 B.					
16.	18·229	19·90	0·4672	−3899 cal.	−3898 cal. at 20°	7287 cal.
17.	17·941	16·95	0·4642	−3926 ,,	−3925 ,, 17	7074 ,,
18.	18·251	14·955	0·4741	−3951 ,,	−3950 ,, 15	6934 ,,
19.	17·979	13·975	0·4699	−3975 ,,	−3975 ,, 14	6846 ,,
20.	18·295	11·965	0·4813	−4001 ,,	−4000 ,, 12	6701 ,,
21.	18·321	9·96	0·4898	−4056 ,,	−4055 ,, 10	6526 ,,
22.	18·143	7·04	0·4925	−4129 ,,	−4130 ,, 7	6271 ,,
23.	18·323	3·935	0·5059	−4199 ,,	−4197 ,, 4	6000 ,,

TABLE Q.—*Heat of Dissolution of Anhydrous Copper Sulphate.*

$CuSO_4 = 158{\cdot}84$; $\frac{3}{40}$ *mol.* = 11·913 *grams.*

	w.	*t*°.	(*t*−*t'*)°.	M at *t*°.	M at T. Whole degrees C.
	Series with Thermometer '08 B.				
1.	11·979	19·965	1·9914	16110 cal.	16112 } 16100 cal. at 20°
2.	11·880	19·97	1·9722	16087 ,,	16099 }
3.	11·958	16·855	1·9644	15918 ,,	15922 ,, 17
4.	11·950	13·375	1·9369	15704 ,,	15711 ,, 13·5
5.	11·999	7·01	1·8851	15219 ,,	15219 ,, 7
6.	11·946	3·945	1·8489	14991 ,,	14996 ,, 4

w.	*t*°.	(*t*—*t*′)°.	M at *t*°.	M at T. Whole degrees C.
		Series with Thermometer '61 B.		
7. 12·009	19·91	1·9909	16070 cal.	16079 } 16089 cal. at 20°
8. 11·853	19·915	1·9679	16093 ,,	16102 }
9. 11·945	16·95	1·9615	15917 ,,	15919 ,, 17
10. 11·937	13·45	1·9358	15717 ,,	15720 ,, 13·5
11. 11·915	7·04	1·8759	15255 ,,	15251 ,, 7
12. 11·894	3·985	1·8371	14966 ,,	14966 ,, 4

TABLE R.—*Heat of Dissolution of Hydrated Copper Sulphate.*

$$CuSO_4,5H_2O = 248·64;\ \frac{3}{40}\ \textit{mol.} = 18·648\ \textit{grams.}$$

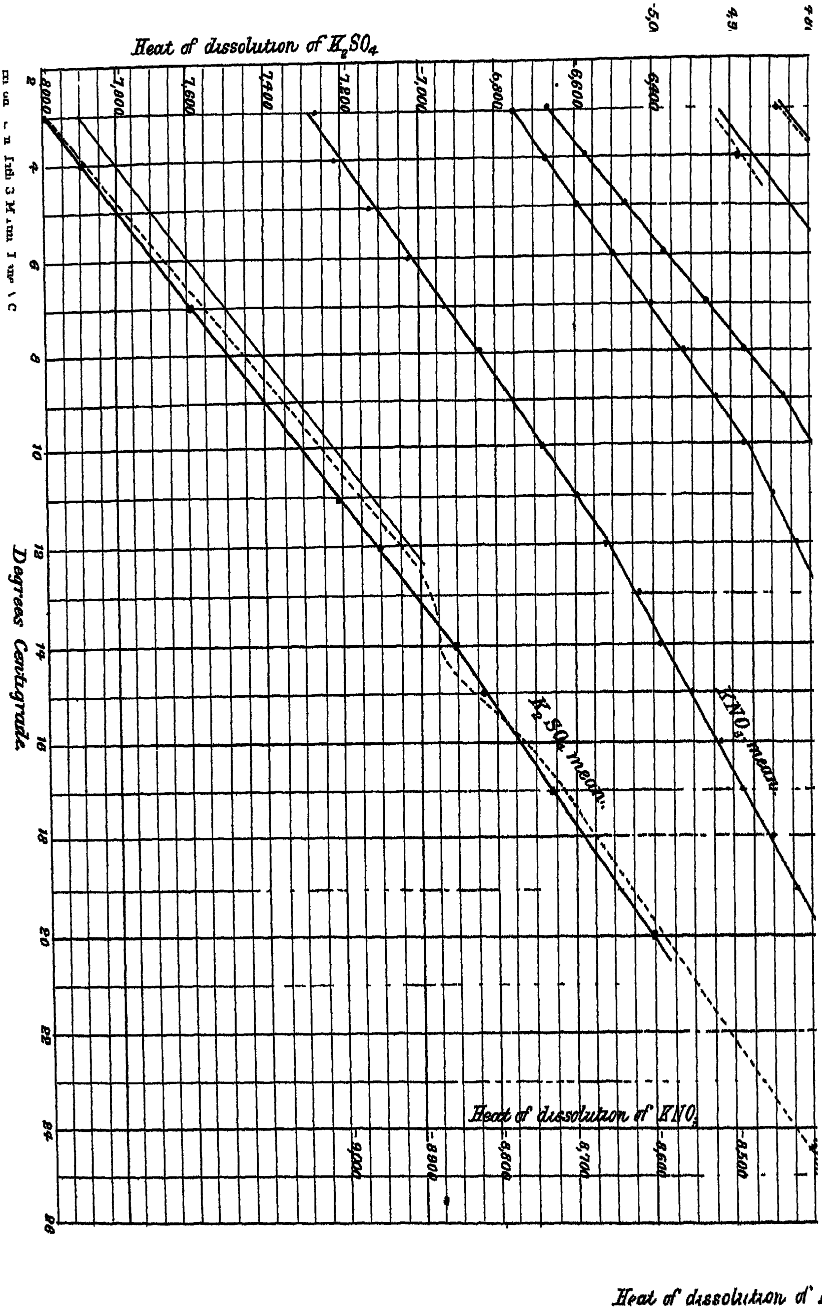
w.	*t*°.	(*t*—*t*′)°.	*m* at *t*°.	*m* at T. Whole degrees C.	M at T.°
		Series with Thermometer '08 B.			
1. 18·905	19·97	0·3351	—2719 cal.	—2718 cal. at 20°	5217 cal.
2. 18·738	16·855	0·3429	—2807 ,,	—2805 ,, 17	5052 ,,
3. 18·873	13·38	0·3542	—2879 ,,	—2877 ,, 13·5	4830 ,,
4. 18·860	7·01	0·3796	—3087 ,,	—3087 ,, 7	4343 ,,
5. 18·852	3·935	0·3929	—3196 ,,	—3192 ,, 4	4106 ,,
		Series with Thermometer '61 B.			
6. 18·935	19·905	0·3359	—2723 cal.	—2720 cal. at 20°	5267 cal.
7. 18·894	16·95	0·3457	—2808 ,,	—2808 ,, 17	5049 ,,
8. 18·930	13·45	0·3522	—2855 ,,	—2854 ,, 13·5	4858 ,,
9. 18·860	7·045	0·3763	—3061 ,,	—3062 ,, 7	4368 ,,
10. 18·736	3·965	0·3859	—3159 ,,	—3158 ,, 4	4140 ,,

XXXIV.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE. No. IX.

Periodates.

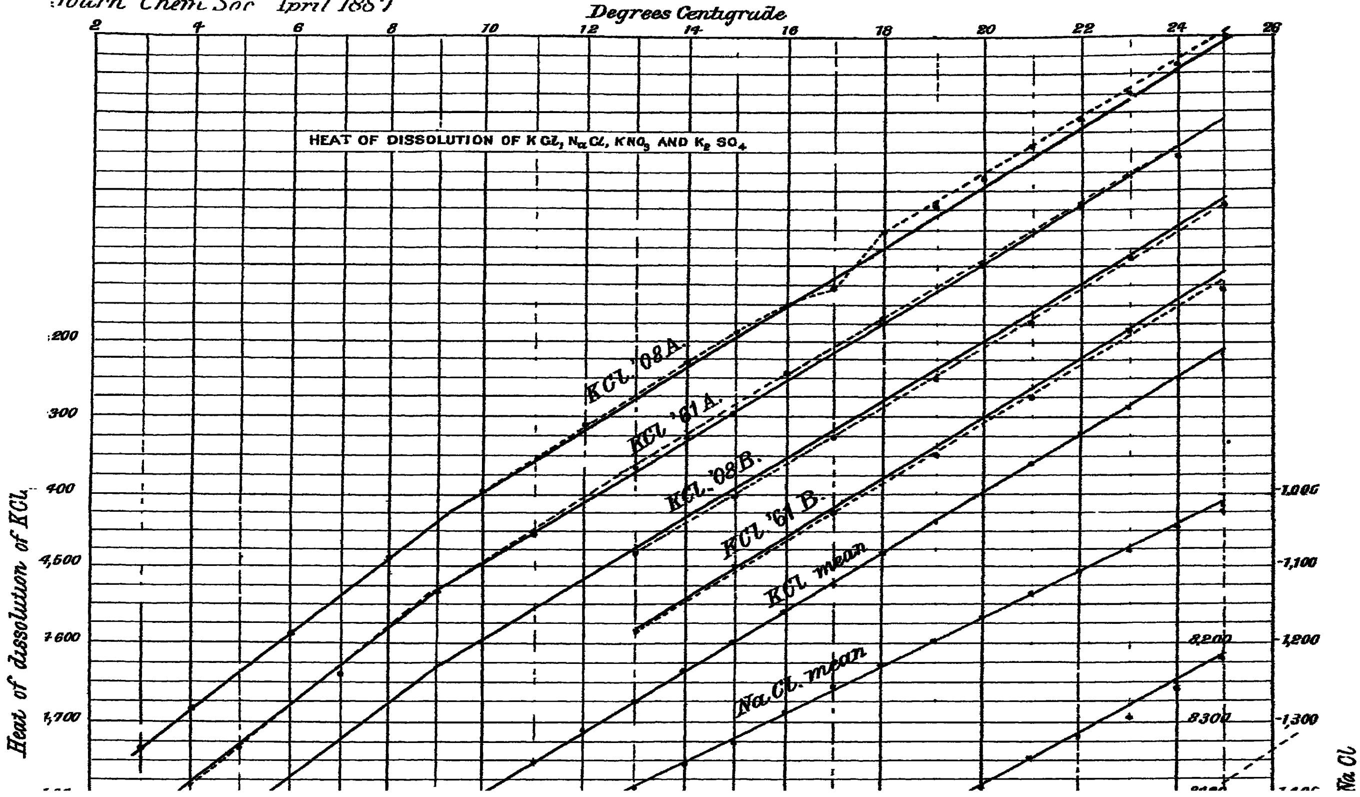
By C. W. KIMMINS, D.Sc., B.A., late Scholar of Downing College, Cambridge.

AT the suggestion of Mr. Pattison Muir, I undertook the preparation and examination of certain periodates of sodium, potassium, and silver, as the results obtained by previous observers are discordant, and the methods of analysis employed by them appear to be faulty. In most cases, the periodates have been analysed by heating them so as to


Heat of dissolution of K_2SO_4
-8000
-7,800
-7,600
-7,400
-7,200
-7,000
-6,800
-6,600
-6,400
-5,0
-4,9
2
4
6
8
10
12
14
16
18
20
22
24
26
Degrees Centigrade.
K_2SO_4 mean.
KNO_3 mean.
Heat of dissolution of KNO_3
-9,000
-8,900
-8,800
-8,700
-8,600
-8,500
Heat of dissolution of

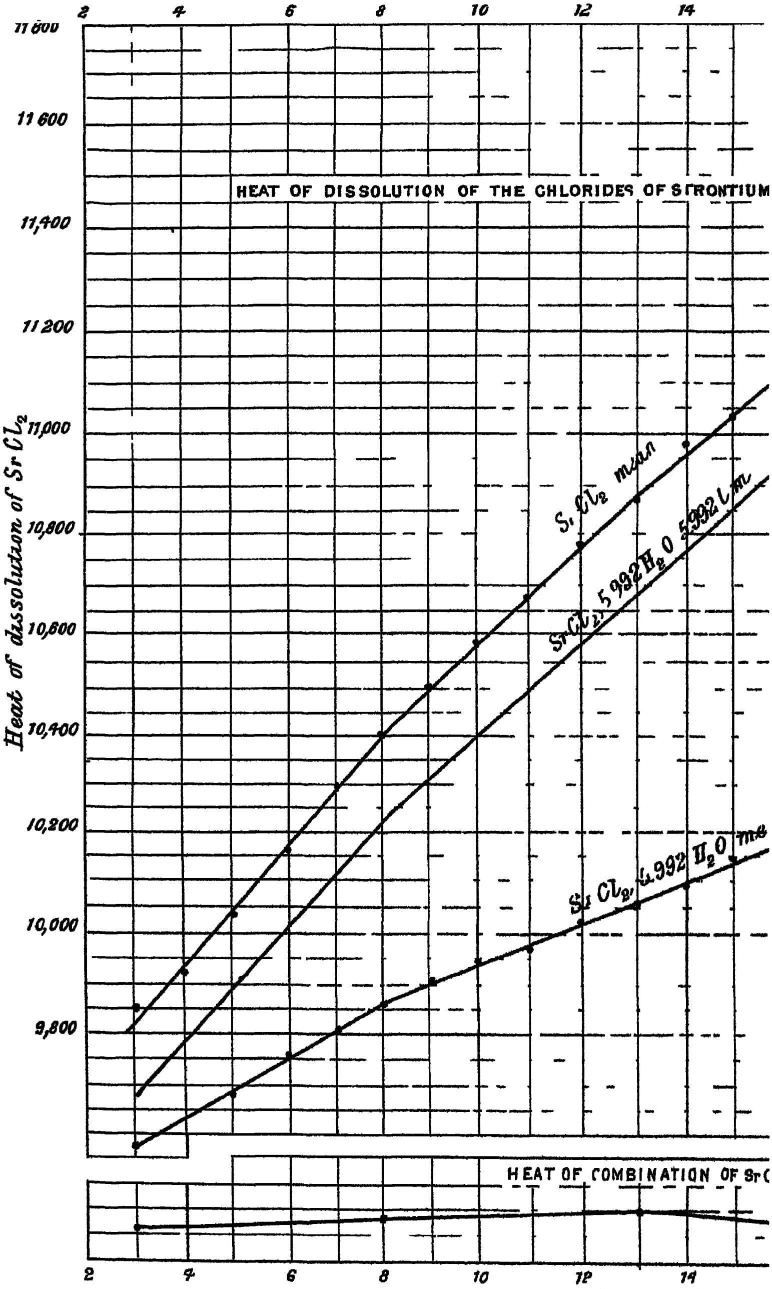
Journ Chem Soc April 1887

Plate 1.



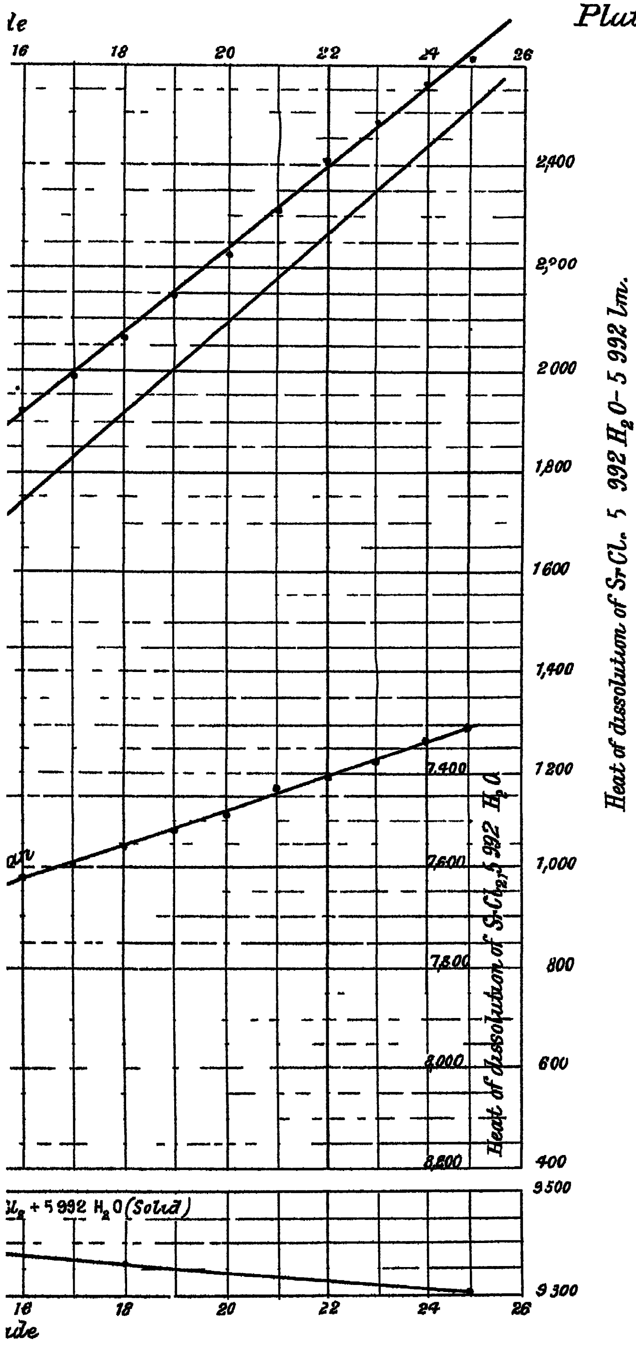
HEAT OF DISSOLUTION OF KCl, $NaCl$, KNO_3 AND K_2SO_4

Journ Chem Soc April 1887



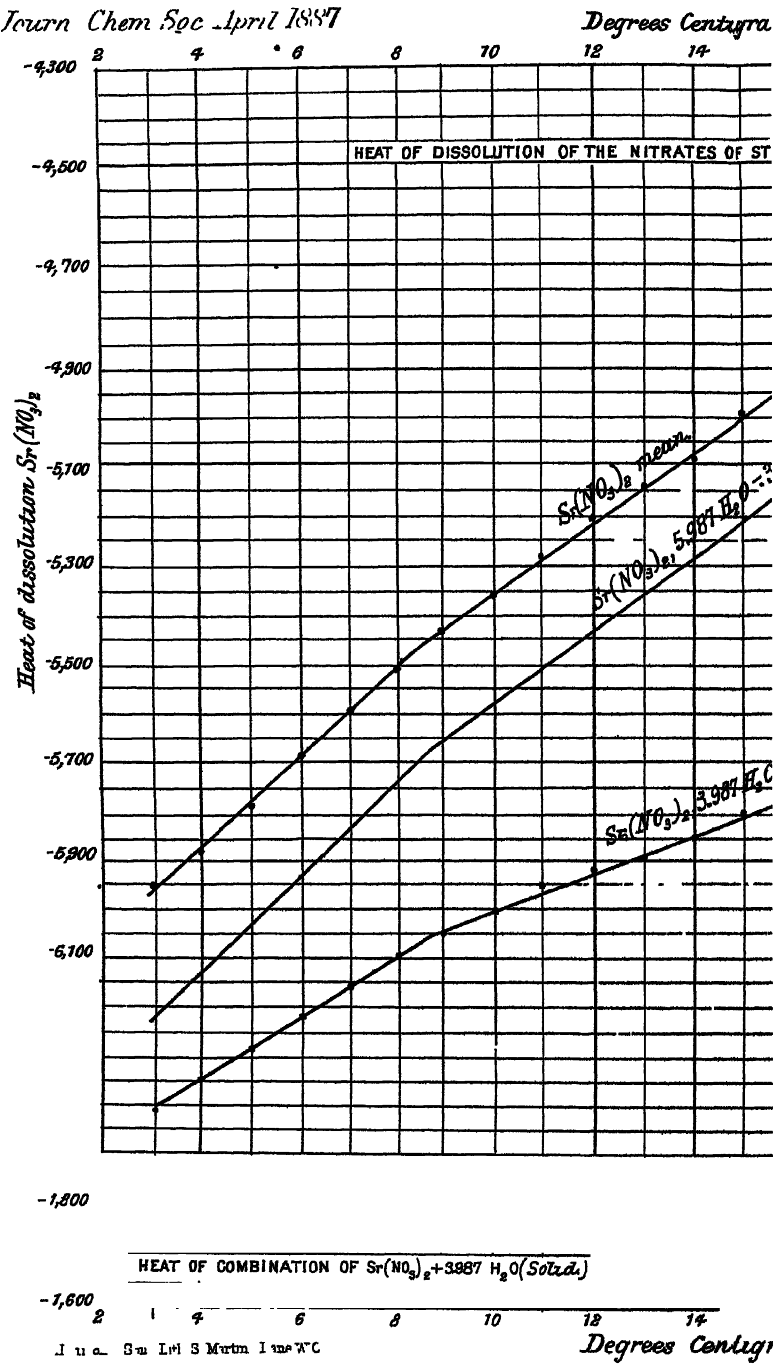
Harrison Sons lith St Martin

Plate 2.



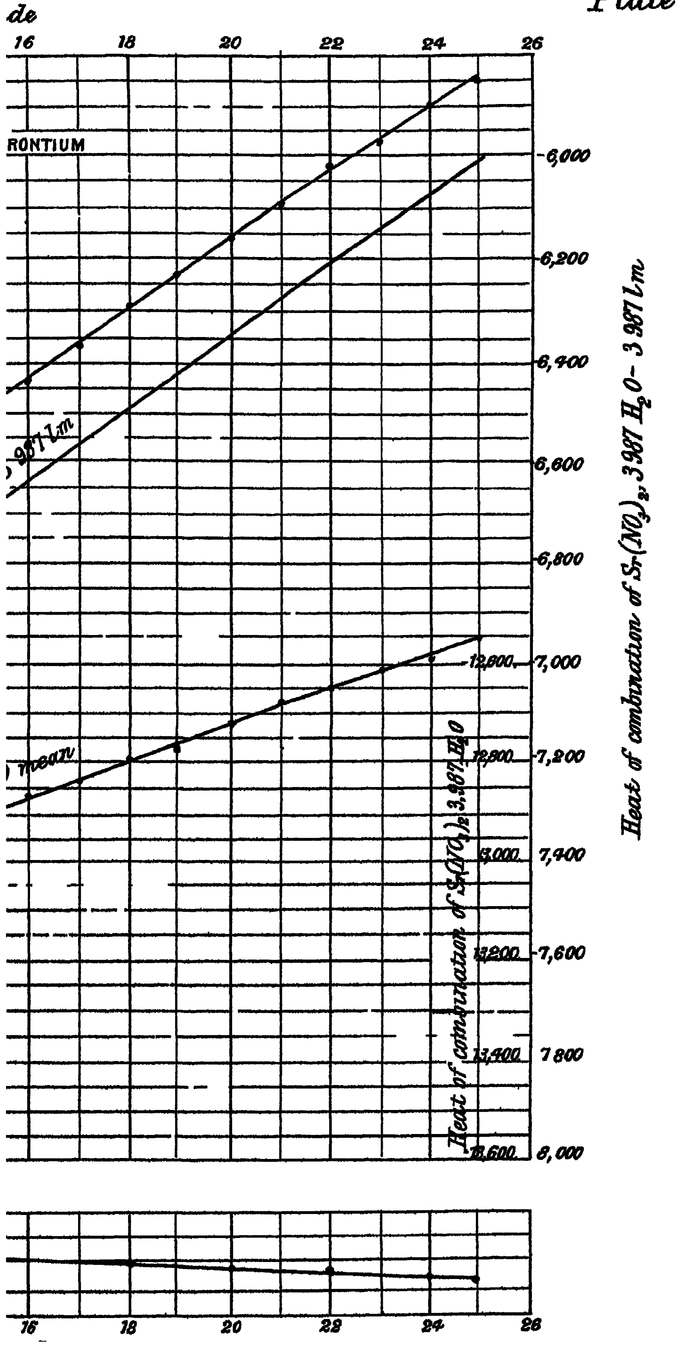
le
16
18
20
22
24
26
2,400
2,200
2000
1,800
1600
1,400
1200
1,000
800
600
400
9500
9300
7,400
7,600
7,800
8,000
8,200
Heat of dissolution of SrCl. 5 992 H2O – 5 992 Lm.
Heat of dissolution of SrCl2, 5 992 H2O
an
Cl2 + 5 992 H2O (Solid)
16
18
20
22
24
26
ude

Journ Chem Soc April 1887



J u a S u Lrl S Murtn I ane A'C

Plate 3


de
16
18
20
22
24
26
RONTIUM
987 Lm
mean
-6,000
-6,200
-6,400
6,600
-6,800
-7,000
-7,200
7,400
-7,600
7 800
8,000
12,600
12,800
13,000
13,200
13,400
13,600
Heat of combination of $Sr(NO_3)_2$ 3.987 H_2O
Heat of combination of $Sr(NO_3)_2$, 3 987 H_2O − 3 987 Lm
16
18
20
22
24
26

Journ Chem Soc April 1887

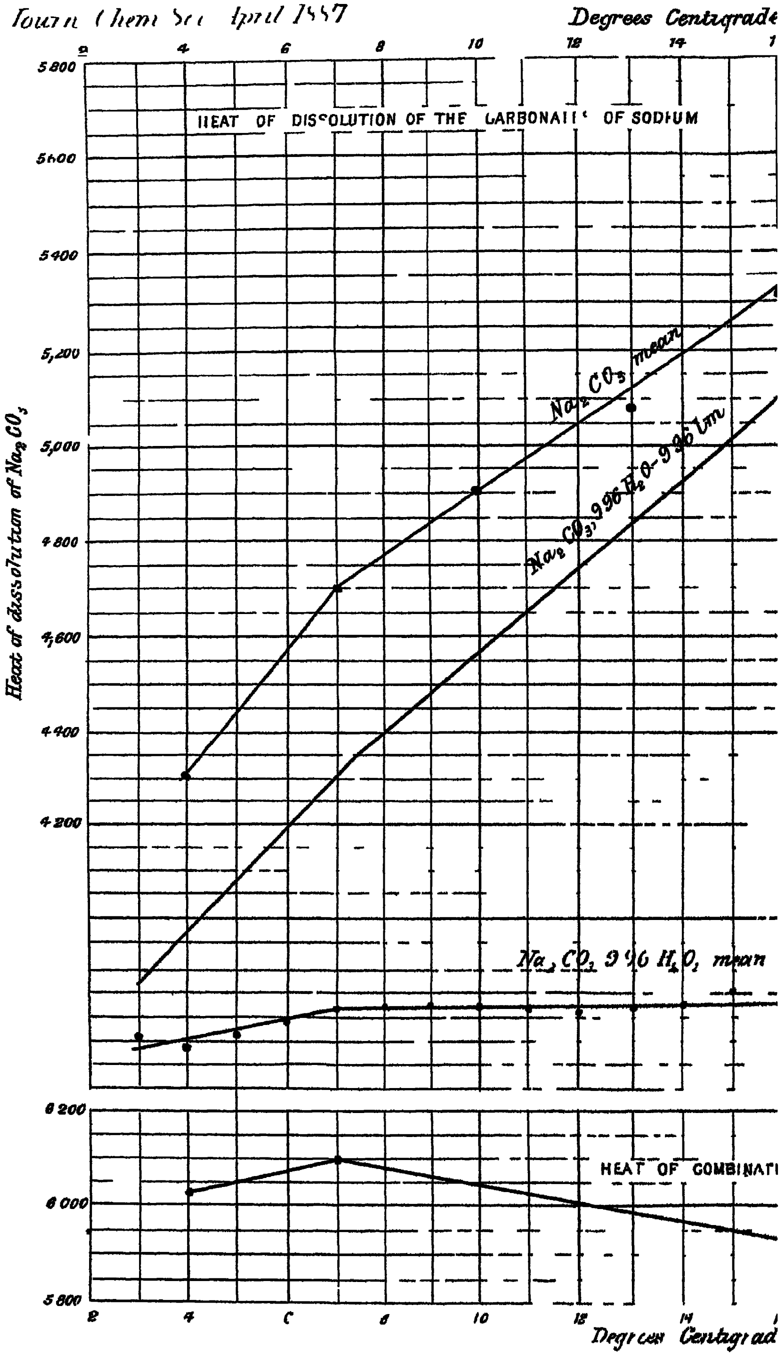
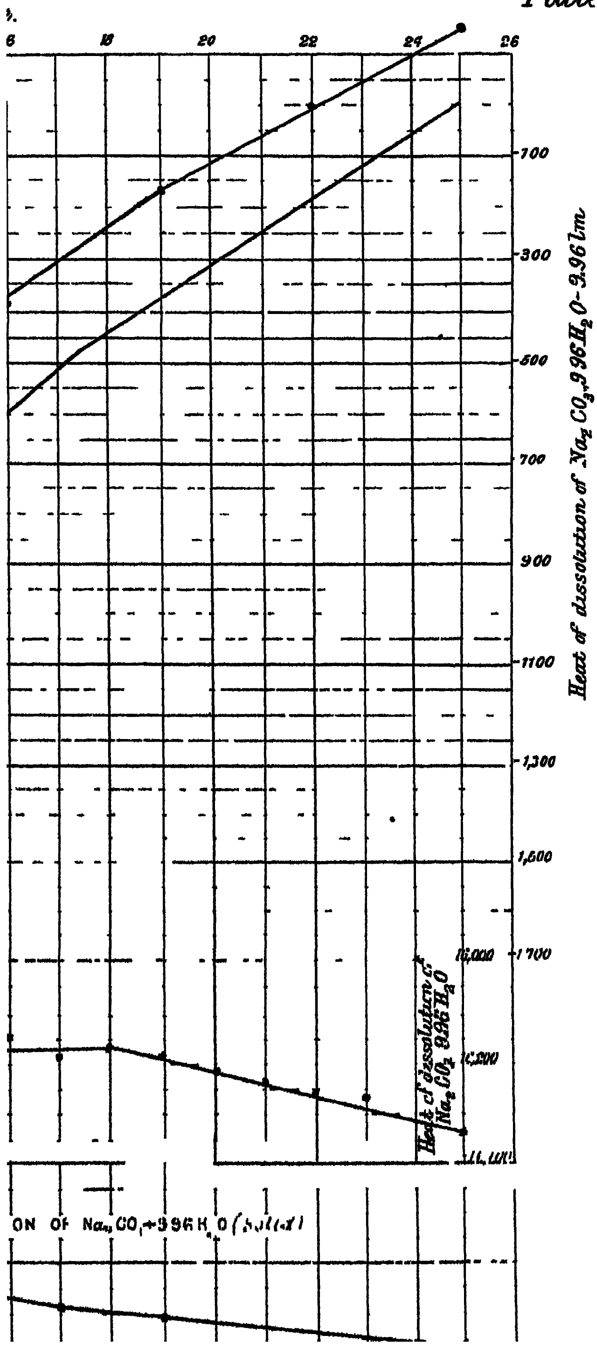
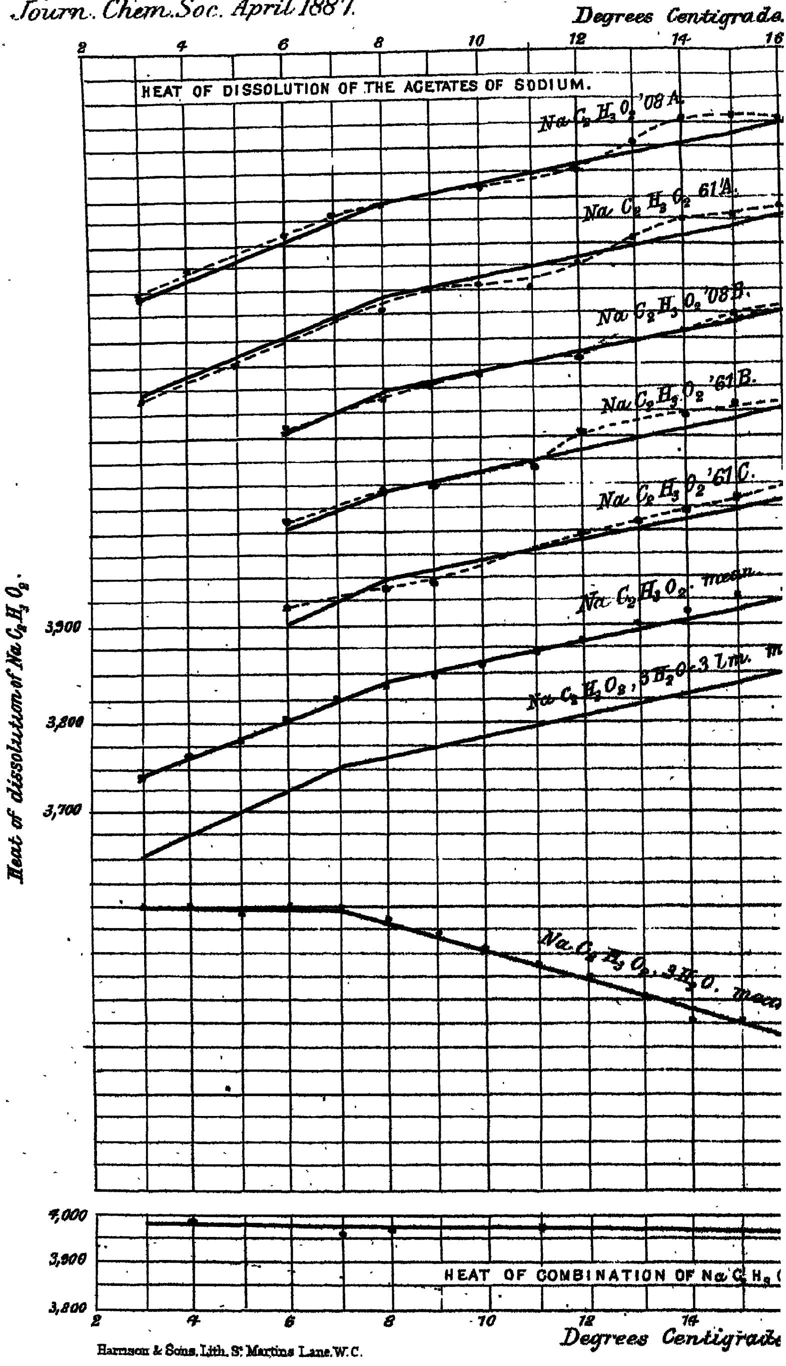


Plate 4

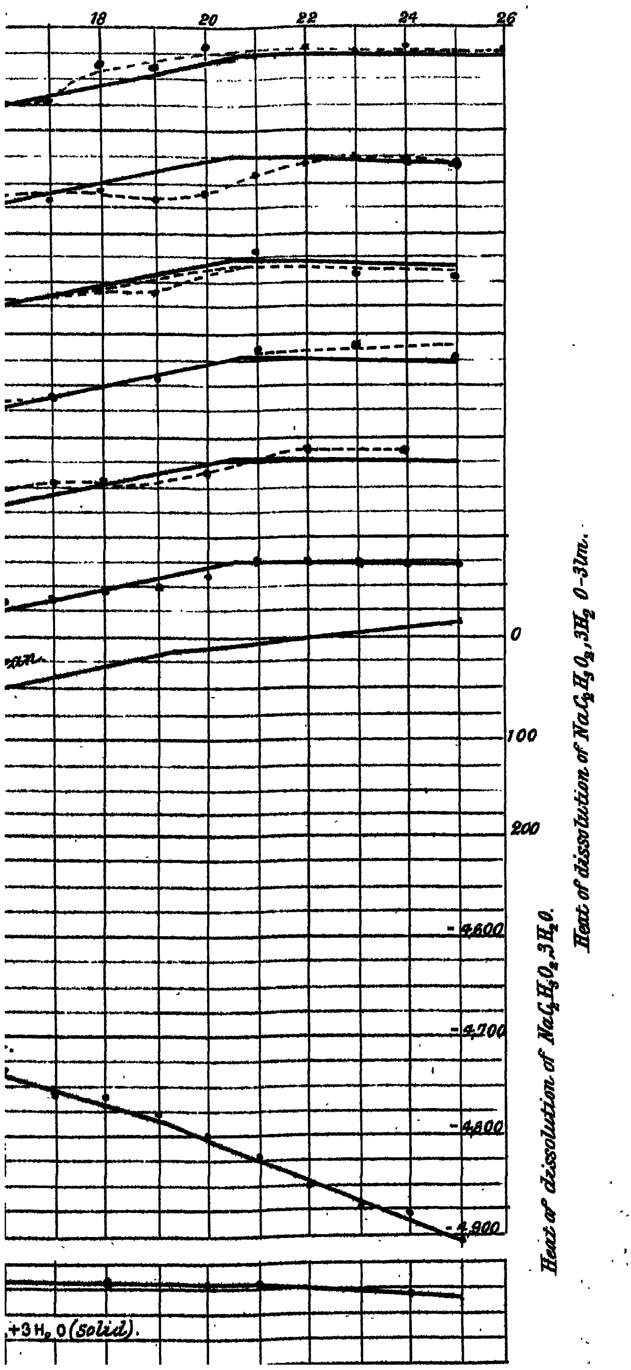


%.
16
18
20
22
24
26
100
300
500
700
900
1100
1,300
1,500
1700
Heat of dissolution of $Na_2CO_3.9.96H_2O - 9.96\,lm$
16,000
16,200
16,400
Heat of dissolution of $Na_2CO_3\ 9.96H_2O$
ON OF $Na_2CO_3 + 9.96H_2O$ (Solid)

Journ. Chem. Soc. April 1887.

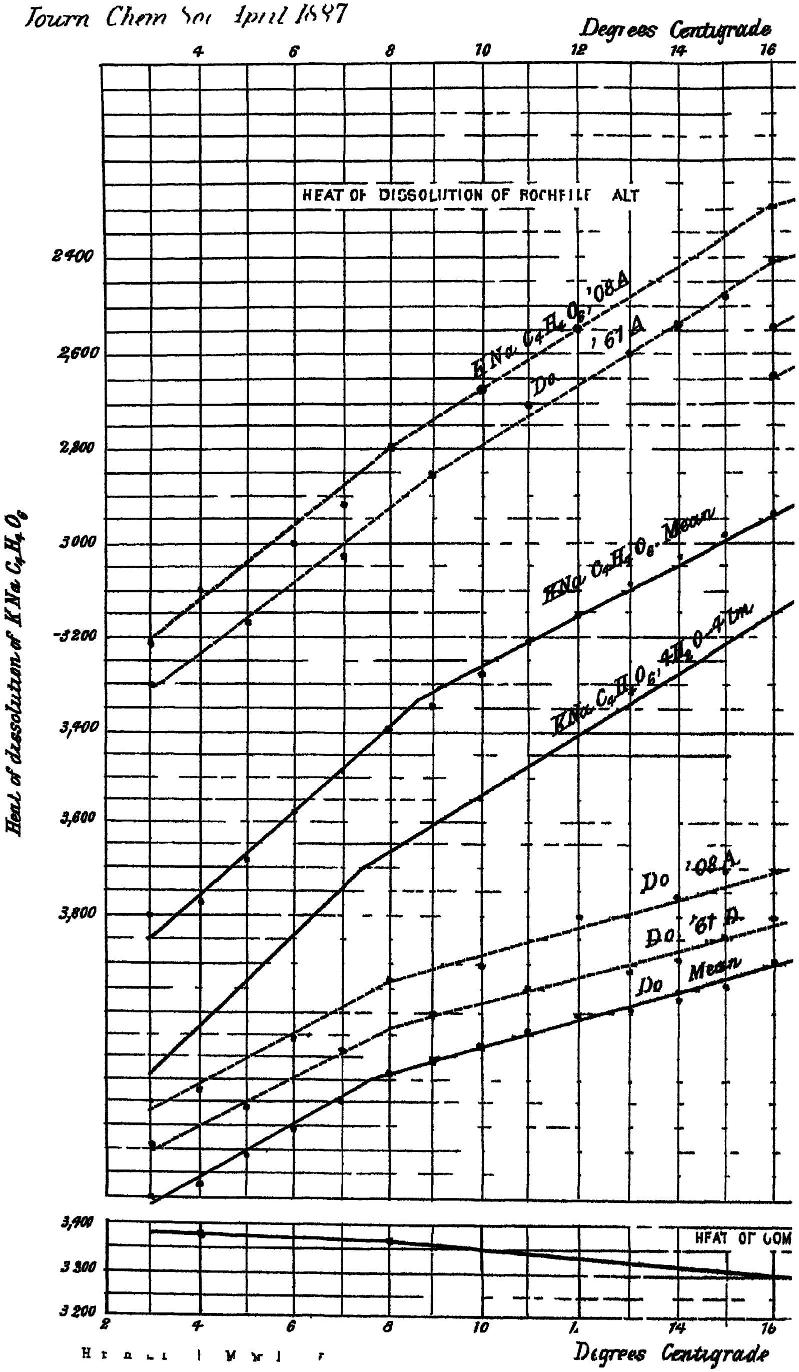


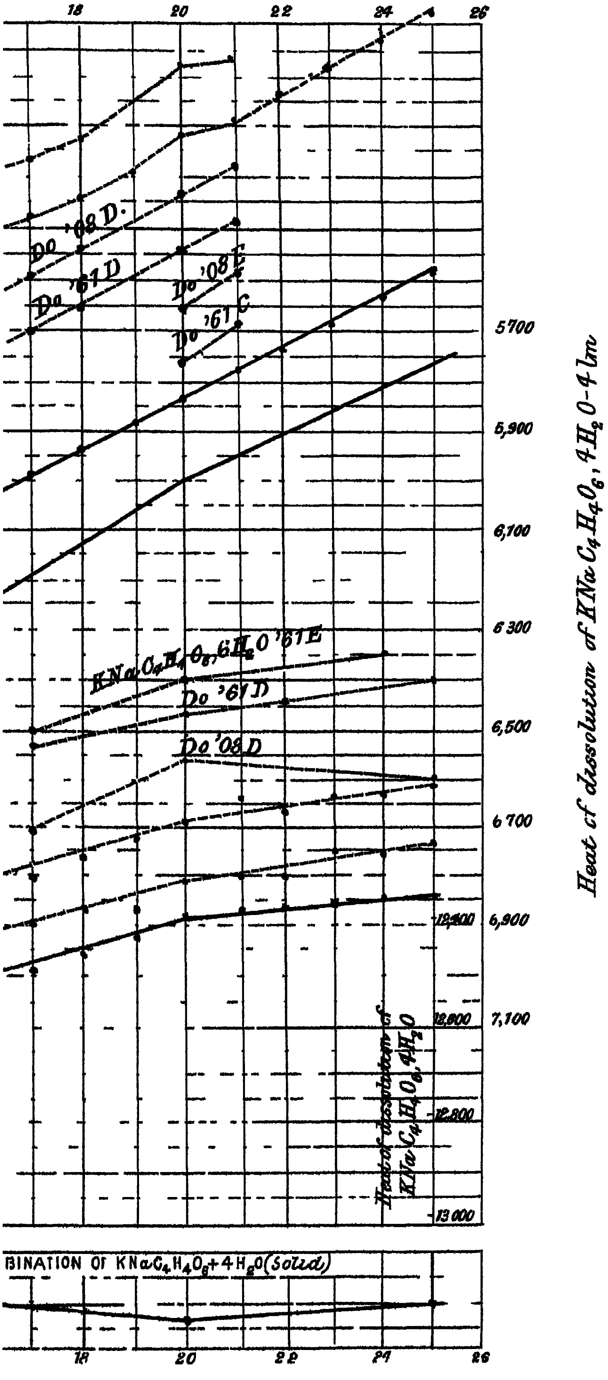
Harrison & Sons, Lith. St Martins Lane. W.C.



18
20
22
24
26
an.
0
100
200
- 4,600
- 4,700
- 4,800
- 4,900
+3 H₂ O (solid).
Heat of dissolution of NaC₂H₃O₂,3H₂O.
Heat of dissolution of NaC₂H₃O₂,3H₂O 0-31m.

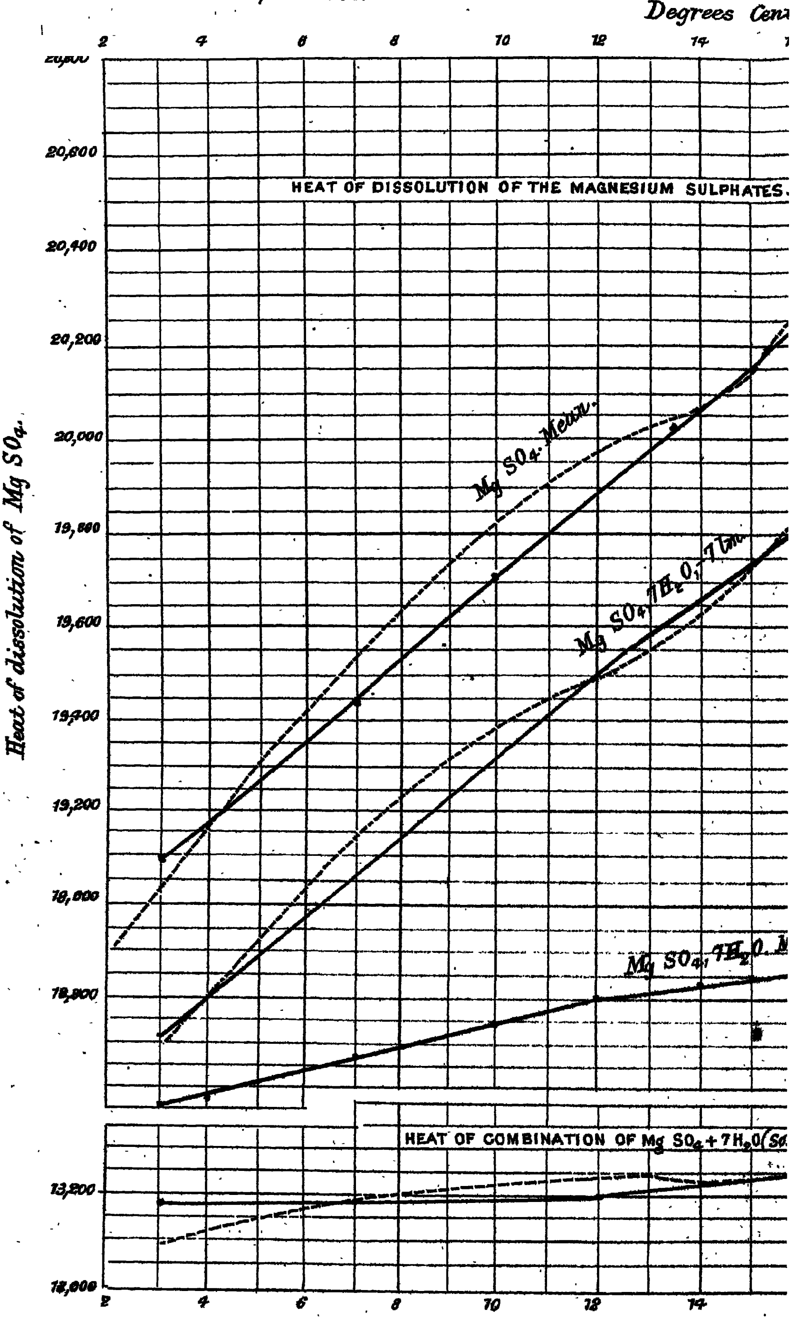
Journ Chem Soc April 1887



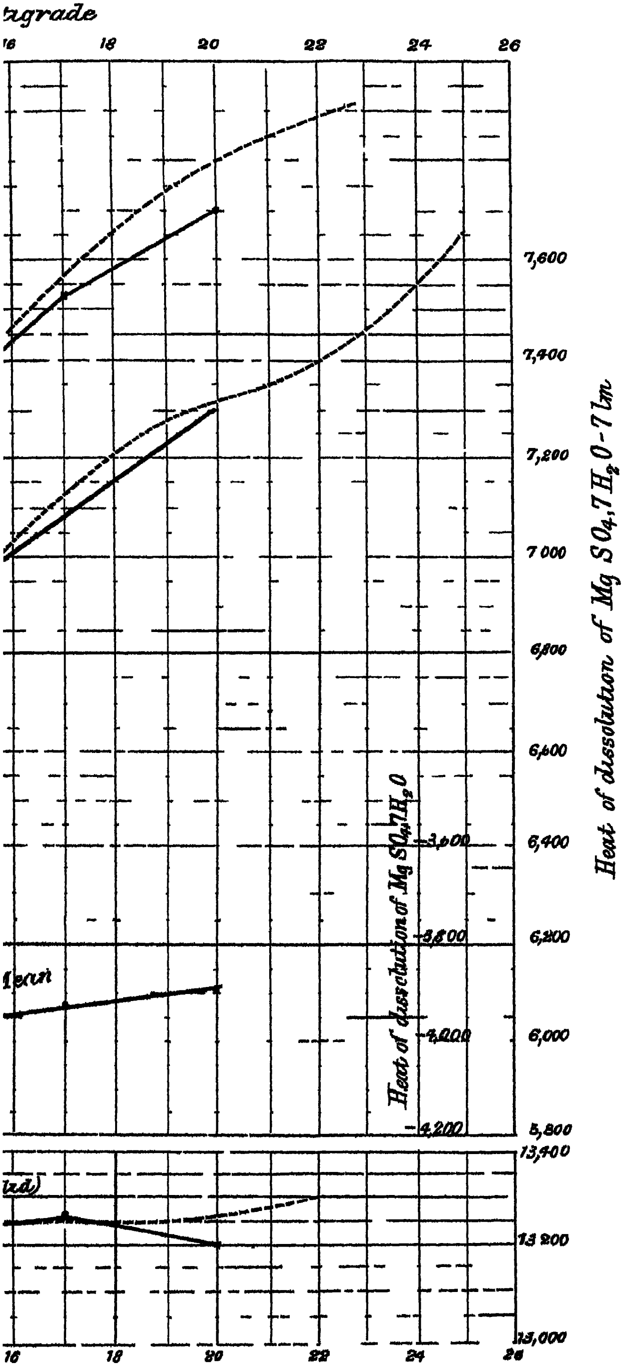


18
20
22
24
26
Do '08 D.
Do '61 D
Do '08 E
Do '61 C
5700
5,900
6,100
6 300
6,500
6 700
6,900
7,100
KNaC4H4O6,6H2O '61 E
Do '61 D
Do '08 D
12,400
12,600
12,800
13 000
Heat of dissolution of KNaC4H4O6,4H2O
Heat of dissolution of KNaC4H4O6,4H2O-4 lm
BINATION OF KNaC4H4O6+4H2O(Solid)
18
20
22
24
26

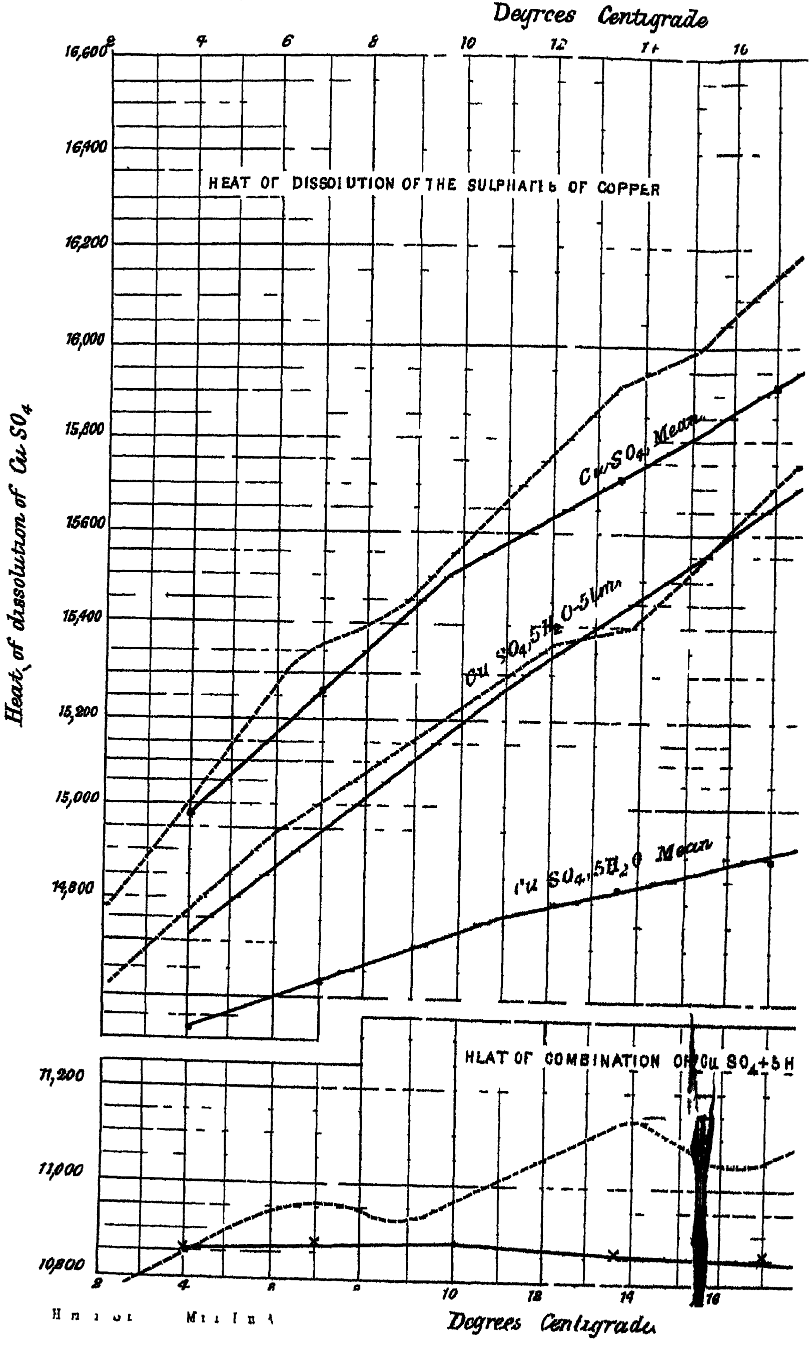
Journ. Chem. Soc. April 1887.

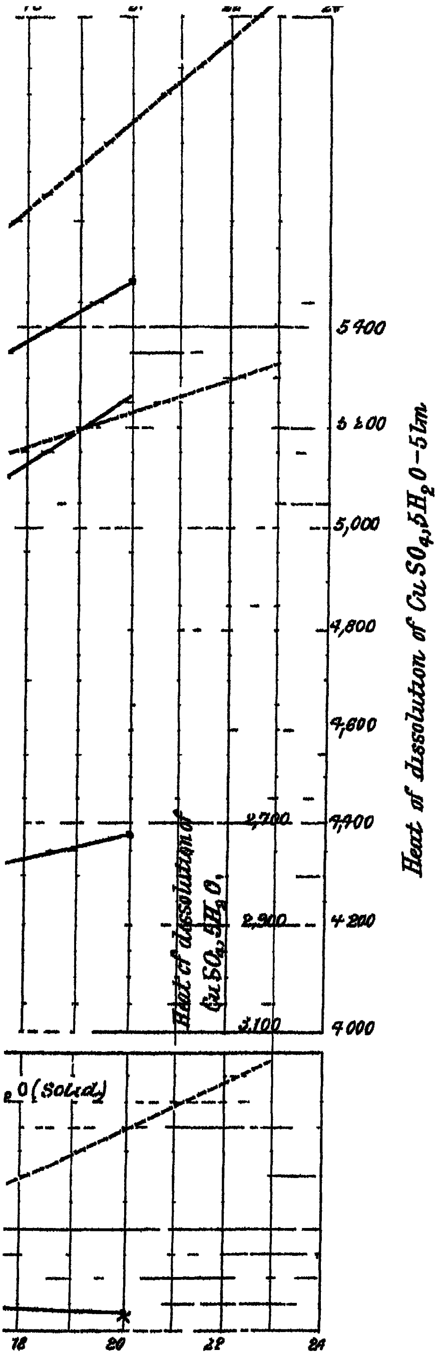


Harrison & Sons. Lith. St Martins Lane. W.C.


tgrade
16
18
20
22
24
26
7,600
7,400
7,200
7 000
6,800
6,600
6,400
6,200
6,000
5,800
13,400
13 200
13,000
Heat of dissolution of Mg SO4,7H2O-7 lm
Heat of dissolution of Mg SO4,7H2O
-3,600
-3,800
-4,000
-4,200
lean
zd)
16
18
20
22
24
26

Journ Chem Soc April 1887





5 400
5 200
5,000
4,800
4,600
4,400
4 200
4 000
3,700
3,900
3,100
Heat of dissolution of CuSO$_4$,5H$_2$O–5Tm
Heat of dissolution of CuSO$_4$,5H$_2$O,
O (Solid)
18
20
22
24

convert them into iodides (in some cases there being also a residue of oxide as in Rammelsberg's analysis of $K_4I_2O_9$), and estimating the metal and iodine in the residue. In this investigation, however, the iodine and metal in the periodates have been estimated directly, thereby obviating any error which might arise from a mistaken view as to the exact nature of the residue obtained on heating (for methods of analysis, see Appendix, p. 361).

Periodates of Sodium.

Langlois (*Ann. Chim. Phys*, **34**, 257), by passing chlorine through a boiling solution of equal weights of caustic soda and sodium iodate, obtained the salt $Na_2H_3IO_6$; although this salt is undoubtedly formed in considerable quantities if the solution is saturated in the cold, I found that when it is concentrated at the boiling point of the mixture, a large quantity of another sodium salt is obtained having the composition $Na_3H_2IO_6$; the latter is a white granular precipitate, less soluble than the di-sodium salt, from which it may be separated by washing with small quantities of water for about 30 hours.

Calculated for $Na_2H_3IO_6$.		Calculated for $Na_3H_2IO_6$.		Found.	
Na..	16·9 p. c.	Na..	23·46 p. c.	Na..	23·66 p c.
I...	46·68 „	I...	43·19 „	I...	42 47 „

With a less concentrated solution, I obtained a mixture of about equal quantities of the salts $Na_2H_3IO_6$ and $Na_3H_2IO_6$.

C. Rammelsberg (*Pogg. Ann.*, **134**, 368, 499) does not mention either of these salts, but states that he obtained the salt $NaIO_4$ on neutralising periodic acid with sodium hydrate. This would point to different thermal relations between the acid and sodium hydrate on neutralisation to those obtained by Thomsen for potassium hydrate.

Periodates of Potassium.

a. KIO_4.—This salt is obtained by a method similar to that used for the sodium salts; but as it is more difficult to obtain in consequence of its greater solubility, it is necessary to concentrate the solution of potassium hydrate and potassium iodate before passing chlorine through it. The salt must be recrystallised repeatedly. My analyses of this salt confirm the results of Magnus and Ammermuller, and of Langlois, who, however, did not estimate the potassium and iodine from the periodate but from the iodide obtained on heating.

b. $K_3HI_2O_9$.—Magnus and Ammermüller say that on concentrating the solution obtained above after removal of KIO_4, a second salt is obtained in small quantity having the composition $K_4I_2O_9$. Langlois does not mention this salt, but Rammelsberg obtained crystals having the composition $K_4I_2O_9,3H_2O$. I have not investigated this salt, although I observed on concentrating the solution that a further crystallisation took place. I found, however, that on adding a very small quantity of nitric acid to a dilute solution of the washings from the precipitate of KIO_4, and to the solution left after crystallising out KIO_4, a well-defined white crystalline precipitate was at once formed, which on analysis was found to have the composition $K_3HI_2O_9$. This salt is much less soluble than KIO_4, and contains no water of crystallisation.

	Calculated for $K_3HI_2O_9$		Found.
K....	22 61 per cent.	K....	22·67 per cent.
I....	49·2 „	I....	48·23 „

Periodates of Silver.

These are best obtained by dissolving the sodium salts in water containing nitric acid, and precipitating with silver nitrate; different salts being formed according to the strength of nitric acid used: I have found it possible in many cases to change the silver salt by decreasing or increasing the strength of acid. The order in which they are formed is as follows:—

(1.) Ag_2HIO_5,
(2.) $Ag_2H_3IO_6$,
(3.) $Ag_3H_2IO_6$,
(4.) $AgIO_4 \cdot H_2O$.

a. Ag_2HIO_5.—If the amount of nitric acid used be just sufficient to effect the dissolution of the sodium salt, a dark-brown precipitate will be formed on adding silver nitrate; this has the formula Ag_2HIO_5.

	Calculated for Ag_2HIO_5.		Found.
Ag....	50·94 per cent.	Ag....	50·82 per cent.
I.....	29·99 „	I.....	28·34 „

It is generally stated that the silver salt prepared in this way has the composition Ag_5IO_6; I have been unable to obtain this salt, however, either by this method or by that given by Rammelsberg, viz., treating $Ag_4I_2O_9,3H_2O$ with silver nitrate in the cold.

b. $Ag_2H_3IO_6$.—This salt is obtained when a slight excess of nitric acid is used in dissolving the sodium salt. It is thrown down as a dark-red precipitate on addition of silver nitrate.

	Calculated for $Ag_2H_3IO_6$.		Found.
Ag....	48·87 per cent.	Ag....	48·85 per cent.
I.....	28·73 „	I.	28·24 „

c. $Ag_3H_2IO_6$.—With a further excess of nitric acid, a slate-coloured precipitate is formed which on analysis appears to have the composition expressed by the formula $Ag_3H_2IO_6$, but the determinations of silver and iodine do not yield satisfactory results owing to the formation of a small quantity of silver iodide which can scarcely be separated from the periodate. In consequence of this, the determination of silver was too low, and that of the iodine too high. I propose to make further experiments on this point.

d. $AgIO_4,H_2O$.—If the sodium salts be dissolved in concentrated nitric acid and treated with silver nitrate, or if the silver salts mentioned above be dissolved in strong nitric acid and evaporated on a water-bath, orange crystals are formed of the formula $AgIO_4,H_2O$. This salt is stated by Rammelsberg and others to be without water of crystallisation. It is very difficult to estimate the water in this salt, as part of the water is given off at the temperature necessary to free the crystals from the last traces of nitric acid, but the whole of the water is not removed until the salt has been kept for some hours in the air-bath at 130°. The results obtained, however, leave no doubt as to the composition of the salt. The change may probably be expressed by the equation

$$Ag_2H_3IO_6 + HNO_3 = AgIO_4,H_2O + H_2O + AgNO_3,$$

the silver nitrate crystallises out on evaporating the nitric acid solution after the separation of the orange crystals.

e. $AgIO_4$.—On keeping the orange crystals for six hours at 130°, a bright yellow powder is formed which has the formula $AgIO_4$.

	Calculated for $AgIO_4$.		Found.
Ag....	36·12 per cent.	Ag....	36·6 per cent.
I.....	42·4 „	I.....	41·45 „

f. $Ag_4I_2O_9,3H_2O$.—On treating the orange crystals, $AgIO_4,H_2O$, with water, periodic acid is formed, and light-yellow crystals which have the composition $Ag_4I_2O_9,3H_2O$. This was proved by direct estimation of the silver and iodine, and also by driving off the water, and estimating the silver and iodine in the dehydrated salt (see below).

g. $Ag_4I_2O_9,H_2O$.—On keeping the light-yellow crystals at 100° for 12 hours, a claret-coloured salt is obtained, which has the formula

$Ag_4I_2O_9,H_2O$, proved by direct estimation of the silver and iodine, and also by analysis of the dehydrated salt.

Loss of water calculated	= 4·08	per cent.
„ „ found	= 4·15	„

Rammelsberg obtained a loss of 5·53 per cent. at 100°; he says that a portion of the third molecule is given off, but I found the weighings to be quite constant after 12 hours, and that no more water was given off until the temperature reached 130°, at which temperature the whole of the water was removed. Rammelsberg also states (*Pogg. Ann.*, **134**, 368) that if the salt with 3 mols. H_2O be first converted into $Ag_4I_2O_9,H_2O$, it then requires a higher temperature—150°—to drive off the last molecule of water.

h. $Ag_4I_2O_9$.—This salt is formed as a chocolate-coloured powder on keeping the claret-coloured salt at 130° for 12 hours.

Loss of water calculated	= 2·12	per cent.
„ „ found	= 2·49	„

Estimation of silver and iodine in the dehydrated salt—

	Calculated for $Ag_4I_2O_9$.		Found.
Ag....	52·04 per cent.	Ag....	52 01 per cent.
I.....	30·6 „	I.....	31·16 „

I have, therefore, prepared and analysed the following silver periodates:—

(1.) Ag_2HIO_5 (dark-brown),
(2.) $Ag_2H_3IO_6$ (dark-red),
(3.) $Ag_3H_2IO_6$ (slate-coloured),
(4.) $AgIO_4,H_2O$ (orange crystals),
(5.) $AgIO_4$ (bright-yellow powder),
(6.) $Ag_4I_2O_9,3H_2O$ (light-yellow),
(7.) $Ag_4I_2O_9,H_2O$ (claret-coloured),
(8.) $Ag_4I_2O_9$ (chocolate-coloured).

The effect of nitric acid in bringing about a change in the silver salts is well shown by its action on Ag_2HIO_5. If this salt is treated with acid not strong enough to completely dissolve it, it is converted into the dark-red and slate-coloured salts which can easily be separated, and on filtering from the precipitated salts, and evaporating the filtrate on a water-bath, orange-coloured crystals of $AgIO_4,H_2O$ are deposited; whilst on further evaporation a small quantity of silver nitrate separates out.

This reaction is probably represented by the following equation:—

$$6Ag_2HIO_5 + HNO_3 + 3H_2O = 2Ag_3H_2IO_6 + Ag_2H_3IO_6 + AgNO_3 + 3AgIO_4,H_2O.$$

On treating the potassium salts with strong nitric acid and silver nitrate, the same silver periodate, $AgIO_4,H_2O$, is produced on evaporation as that formed from the sodium salts. I am at present investigating the nature of the intermediate compounds, and also the effect of heat on the periodates, to see whether it is possible by this means to pass from a member of one series to a member of another, as from H_5IO_6 to H_3IO_5. These results, together with analyses of periodates of other metals, I hope to communicate in another paper, when it may be possible to criticise the existing scheme of classification of these compounds.

I must express my thanks to Mr. Pattison Muir for continued help and suggestions during the course of these experiments.

Appendix.

Methods of Analysis.—The sodium and potassium were estimated in the usual way as sulphates, and the silver as chloride.

The iodine was estimated by a method similar to that used for determining this element in iodates. A weighed quantity of periodate was treated with a concentrated solution of potassium iodide and excess of strong hydrochloric acid in a bottle with a well-fitting stopper, which was immersed in boiling water for six hours; the iodine was then titrated with sodium thiosulphate. One-eighth the quantity so found represents the amount present in the given weight of the periodate.

In order to test this method, I prepared some pure barium periodate by passing air over heated barium iodate, the amount obtained being within 0·1 per cent. of that required by equation:—

$$5Ba(IO_3)_2 = Ba_5I_2O_{12} + 4I_2 + 9O_2.$$

This salt, and a silver salt of known composition, gave results agreeing within 0·2 per cent. of the amount required by calculation.

The best results are obtained with about 0·3 gram of the sodium or potassium salt and 0·5 gram of the silver salts, in a bottle of about 250 c.c. capacity. The action is quite complete after keeping the mixture at 100° for six hours.

XXXV.—*On Tartaric and Racemic Acids, and the Magnetic Rotation of their Ethereal Salts.*

By W. H. PERKIN, Ph.D., F.R.S.

IN 1867, I laid before the Society an account of some experiments on the basicity of tartaric acid (*J. Chem. Soc.*, **20**, 148, 149), in which I described some derivatives of tartaric and racemic acids which could be distilled; and from the fact that these boiled at about the same temperature, I inferred that the molecular weight of both acids must be the same, notwithstanding the fact that racemic acid is built up of dextro- and lævo-tartaric acids, and can be separated into them again. Since then, a good deal of work has been done upon those compounds, and more recently Anschutz and Pictet have not only re-examined some of the compounds I previously described, but have also prepared new ones. They have also shown that ethyl tartrate when pure can be distilled, and that tartrate and racemate of methyl have practically the same boiling points (*Ber.*, **13**, 1177—1178).

As magnetic rotary polarisation has been found capable of detecting even small difference of constitution in substances, I was induced to examine some of the compounds of tartaric and racemic acids by this method, to see if any fresh light could be obtained in reference to them. The products I used for this purpose were the ethylic derivatives.

As is well known, the preparation of the neutral ethers of these acids is troublesome. In my experiments I employed the usual method of saturating the alcoholic solution of the acids with hydrochloric acid, allowing the mixture to stand, and then resaturating. (In one operation I used sulphuric acid, but it did not appear to act any better, if so well as hydrochloric acid.) Some of the alcohol and the hydrochloric acid were then removed by distillation on the water-bath, the product mixed with ether, and the mixture washed first with a little water, and afterwards with dilute sodium carbonate solution; it was then dried over potassium carbonate, the ether distilled off, and the residue fractioned under reduced pressure. This last operation was found to be very troublesome, owing to the frothing of the product; it was stopped when decomposition set in. After the first distillation, the ethers could be redistilled under reduced presure without much difficulty, and two or three fractionations were sufficient to obtain them with almost constant boiling points.

The tartrate and racemate of ethyl obtained in this way were colourless liquids, viscid, like glycerol. They both boiled at the same temperature, viz., 232—233° (corr.) at 197 mm.

The permanent rotation of this tartaric ether was found to be as follows:—

t.	α (l = 200 mm.)	$[\alpha]_D$.
12°	+ 17·5	+ 7·220
14	18·1	7·481
16	18·56	7·658
18	18·97	7·807
20	19·30	8·017

These results show how sensitive the rotation of this ether is to changes of temperature, as pointed out in Amé Pictet's Dissertation, *Recherches sur les Éthers Tartariques* (Geneva, 1881). My results come somewhat higher than his, which for 20° are α 18·47 and $[\alpha]_D$ = 7·659.

The relative density determinations gave—

Tartaric ether ..	$d^{15°}_{15°}$ 1·2097	$d^{25°}_{25°}$ 1·2019,
Racemic ether...	$d^{15°}_{15°}$ 1·2098	$d^{25°}_{25°}$ 1·2021.

Anschutz and Pictet found for tartaric ether at 14°, 1·2097, but it does not appear whether this is given as the relative or the true density (*Ber.*, 13, 1177).

The following are the results of the observations on the magnetic rotation of these bodies:—

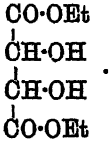
Tartaric Ether.

	t°.	Sp. rot.	Mol. rot.
	16·5°	0·9241	8·751
	16·5	0·9250	8·759
	17·0	0·9289	8·799
	17·0	0·9308	8·818
	13·0	0·9385	8·864
	13·0	0·9177	8·670
	13·5	0·9252	8·744
	13·5	0·9243	8·736
	14·0	0·9257	8·752
	14·0	0·9259	8·774
Average..	14·8	0·9266	8·766

Racemic Ether.

t°.	Sp. rot.	Mol. rot.
17·5°	0·9241	8·755
17·5	0·9329	8·839
18·0	0·9182	8·702
18·5	0·9270	8·786
18·5	0·9234	8·754
13·4	0·9230	8·722
13·4	0·9238	8·729
13·8	0·9229	8·724
13·8	0·9248	8·741
14·0	0·9251	8·745
14·0	0·9264	8·758
13·0	0·9260	8·748
15·5	0·9248	8·759

From the above results we see not only that the boiling points and densities of tartaric and racemic ethers are identical, but that this is also true of the magnetic rotation. This latter is remarkably close to that which we should expect from the formula—



$$\begin{array}{l}\mathrm{CO{\cdot}OEt}\\ |\\ \mathrm{CH{\cdot}OH}\\ |\\ \mathrm{CH{\cdot}OH}\\ |\\ \mathrm{CO{\cdot}OEt}\end{array}.$$

This is seen if we take the magnetic rotation of succinic ether, and add to it the values of two oxygens, as found for those in glycol (Trans., 1884, 515 and 559).

Ethyl succinate	8·380
O_2	0·389
	8·769

That tartaric and racemic ethers should have the same properties is perhaps not astonishing, because we know that racemic acid when converted into certain salts, forms not one salt, but those of right- and left-handed tartaric acids, so that when etherified it is not unlikely that it also should yield ethers of right- and left-handed tartaric acids, and this is what appears to happen. The difficulty of preparing left-handed tartaric acid has prevented me from examining it separately.

There is one marked difference between tartaric and racemic acid, and that is that the latter always crystallises with a molecule of water, and the question arises as to whether this be water of crystallisation or part of the molecule, because it is quite easy to represent racemic acid as a single molecule derived from two of tartaric acid, with the elements of two molecules of water, and as racemic ether does not represent the ordinary crystallised racemic acid, but the compound from which water has been separated, this possibly might account for its being a mixture of the ethers of the two tartaric acids.

As most neutral silver salts are void of water of crystallisation, I had the curiosity to prepare the silver salts of tartaric and racemic acids direct from the acids themselves, by adding rather strong aqueous nitrate of silver to their moderately concentrated solutions; the salts, which were quickly formed, were filtered off, washed, and *air*-dried. They were, however, found to have the ordinary composition $C_4H_4Ag_2O_6$.

The densities of comparable solutions of tartaric and racemic acid were next examined, because if right- and left-handed tartaric acids are identical in properties, as we have every reason to believe they are (except as regards polarised light), racemic acid, if simply consisting of these united in virtue of their crystalline natures, would be expected to give when dissolved solutions of the same density as tartaric acid; on the other hand, if derived from the two tartaric acids plus the elements of water, it would be expected to give solutions dissimilar in density.

In the first determinations, rather dilute solutions were taken, the proportions of 1 mol. of tartaric acid to 100 mols. of water being employed, the same were used with dehydrated racemic acid, but with the crystallised acid only 99 mols. of water, as the acid itself contains one. These solutions contained 8·333 per cent. $C_4H_6O_6$.

The numbers obtained were as follows:—

	t.	I.	II.	III.
Racemic acid (dehydrated)	$\frac{15^\circ}{15^\circ}$	—	1·03714	1·03707
„ crystallised	„	1·03716	—	—
Tartaric acid	„	1·03703	1·03704	1·03701

Average.

$$\left.\begin{array}{l} 1\text{·}03712 \\ 1\text{·}03703 \end{array}\right\} \text{diff.} = 0\text{·}00009.$$

This difference is almost *nil*, but still it was found in all the experiments. These were made side by side, so as to get the same temperature, and the density tubes used were in the last experiment reversed, so that any error arising from the determination of their capacity might be neutralised; this was done also in the subsequent density determinations.

To see if this was a real difference, stronger solutions were used, but as crystallised racemic acid only dissolves to the extent of 1 in 4·84 per cent. of water at 20°, it is of course difficult to get strong solutions; however, by making a hot 25 per cent. solution of the dehydrated acid, and determining its density before it had time to crystallise, the following results were obtained, as compared with tartaric acid solution of the same strength:—

	$t.$	I.	II.	Average.
25 p. c. solution of racemic acid, dehydrated	$\frac{15\cdot3^\circ}{15^\circ}$	= 1·12393	1·12404	1·12398
25 p. c. tartaric acid	$\frac{15\cdot3^\circ}{15^\circ}$	= 1·12333	1·12360	1·12346
			Diff.........	0·00052

Here we find that there is a slightly higher density in the case of racemic acid; the comparison, however, is not a rigorous one, because we are comparing a supersaturated solution of racemic acid with an unsaturated solution of tartaric acid, but although the difference is proportionally larger than in the case of the dilute solutions, still both lay in the same direction.

These results made it desirable to determine the densities of the solid acids. For this purpose they were powdered for use. Toluene was the liquid used in the experiments, and the air was removed from the powdered acid and hydrocarbon by means of the air-pump. The following results were obtained, about 21 grams of acid being used in each case.

Recrystallised racemic acid ($C_4H_6O_6H_2O$)..........	$d\frac{7^\circ}{4^\circ}$	1·6873,	
Dehydrated racemic acid, $C_4H_6O_6$	,,	1·7782	Diff. = 0·0188.
Recrystallised tartaric acid, $C_4H_6O_6$	,,	1·7594	

These numbers show that racemic acid (dehydrated) has a density considerably greater than tartaric acid, viz., 0·0188.

Now, 25 p. c. of this difference is equal to 0·00470,
and 8·33 ,, ,, ,, ,, 0·00154.

The differences in the densities of the solutions of racemic and tartaric acids given above are very small as compared with these.

These results, therefore, lead to the inference that racemic acid when dissolving in water separates into the two tartaric acids, a small quantity only remaining associated, even in supersaturated solutions.

To see whether racemic acid could exist as a definite body if devoid of this molecule of water, a quantity of the ordinary acid crystallised from water, was recrystallised from absolute alcohol. It was thus obtained in well-defined small transparent crystals, differing from tartaric acid in being much less soluble in alcohol. The crystals were dried between bibulous paper, and when heated at 100° neither lost weight nor did they become opaque, so that racemic acid is a definite product without the molecule of water it usually contains. This fact taken in conjunction with those above, point to the conclusion that the water which is given off on drying racemic acid at 100° exists as such in that substance, and is present as water of crystallisation only.

Mr. Pickering has very kindly determined the heat of dissolution of tartaric and racemic acids for me. The following are his results and remarks.

" The acids were dissolved in 400 gram-molecular proportions of water at an initial temperature of 8·77° ± 0·04. The results were as follows: *w* being the weight of the acid taken, and $t - t'$ the fall of temperature observed. The water equivalent of the calorimeter and its contents was 607·74 grams with the anhydrous acids, and 608·74 grams with hydrated acid, the molecular weights taken were 149·64, and 167·6 in the two cases.

Substance.	*w*.	$(t-t')$° C.	Molecular heat of dissolution.	
	grams.			
Tartaric acid (dextro-)	12·506	0·4741	−3447	− 3154
	12·418	0·4729	−3161	
Racemic acid, anhyd.	12·520	0·7836	−5692	− 5675
	12·583	0·7828	−5658	
Racemic acid, hyd. . .	13·956	0·9591	(−7012)	−7065
	14·042	0·9742	−7078	
	14·117	0·9794	−7079	

these numbers agree fairly well with those obtained by Berthelot and Jungfleisch, at 10°.

Tartaric acid	−3270 cal.
Anhydrous racemic acid	−5420 "
Hydrated " "	−6900 "

but Thomson gives a somewhat higher value for the first of these acids, −3596 cal. at 19·6°.

"The heat of dissolution of hydrated racemic acid corrected for the heat of fusion of the water it contains (1501 cal.) is −5564 cal., and the difference between this quantity and the heat of dissolution of the anhydrous acid gives the heat of combination of the latter with its water, this is a negative quantity, −111 cal.; Berthelot's figures give a value not differing very much from this, namely, +68 cal. This value, it must be remembered, refers solely to the heat of combination of the substances in the solid condition, and is independent of any decomposition which they may undergo on dissolution, provided the anhydrous and hydrated acids yield identical solutions, which there is no reason to doubt. Now it is very improbable that the heat of combination of a salt with its water should be a negative quantity or even *nil*, there is indeed but one imperfectly established case in which the experimental results indicate such an occurrence (this vol., p. 77); it is more probable that the negative value is apparent not real. Two explanations may be offered: first, that the so-called hydrated acid does not contain water of crystallisation at all, but an additional $H_2 + O$ as part of its constitution.* The general behaviour of the acid, however, tends to discountenance such a view, especially as the molecular volume of the water deduced from Dr. Perkin's results is 16·8, a quantity smaller than that (18·8) of $H_2 + O$, but similar to some of the values found for water of crystallisation in feebly hydrated salts. The second and more probable explanation is that the hydrated acid is not the hydrate of the anhydrous acid, but that when the former is deprived of its water, the residual constituents enter into a state of more intimate combination, the resulting anhydrous compound being different in constitution from the hydrated compound. The quantity, −111 cal., would thus represent the heat of combination of the water, less that absorbed on the alteration of structure accompanying hydration."

Ethyl Diaceto-tartrate and Diaceto-racemate.

Whilst making these experiments on tartaric and racemic acids, I thought it would be of interest to re-examine diacetotartaric and diaceto-racemic ethers in reference to their boiling points. As the temperature at which these boil under ordinary pressure is very high, I preferred to take their boiling points under reduced pressure. They were both found to boil at the same temperature, viz., 229—230°

---

* If it is not water, the heat of formation of the so-called hydrated acid from the anhydrous acid and water will be (7065—5675 =) 1390 cal., no allowance having to be made for the heat of fusion of any water in the first acid.

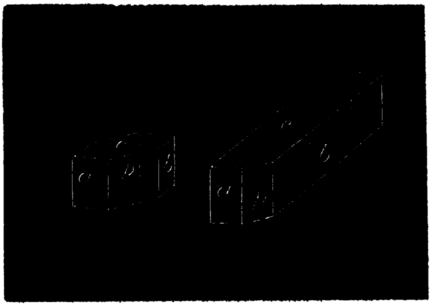
under 100 mm. Whilst preparing diaceto-racemic ether I succeeded in obtaining it in well-defined crystals from a solution in light petroleum. Professor Haushöfer has been so kind as to measure them for me, and obtained the following results:—

Crystalline System Triclinic.

Colourless, but not transparent, crystals in the form of thick tables or plates, the surfaces of which were insufficient for calculating the morphological elements. They appear to be a combination of the three pairs of surfaces (100) = *a*, (010) = *b*, and (001) = *c*, parallel to the axial planes with a hemipyramid (110) = *p*, the different developments of which are represented by the two figures in the cut. The substance is well characterised by the fact that convergent polarised light on the surface *b* gives rise to a uniaxial interference image (somewhat excentric).

Angles measured.

$(0\bar{1}0)(100) = b' : a = 92° \ 26'$
$(0\bar{1}0)(110) = b' : p = 53 \ \ 55$
$(0\bar{1}0)(001) = b' : c = 96 \ \ 45$
$(100)(001) = a : c = 99 \ \ 40$
$(001)(110) = c : p = 93 \ \ 34$



The crystalline form of the diacetotartaric ether has already been measured by M. Ch. Soret, and described in M. Amé Pictet's Dissertation, *Recherches sur les Éthers Tartariques* (Geneva, 1881).

Acid Tartarate of Silver.

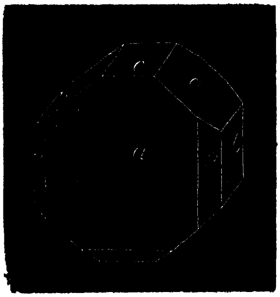
When preparing the tartarate of silver already referred to, by adding a somewhat strong solution of silver nitrate to a similar solution of tartaric acid, after filtering off the silver salt, and allowing the clear solution to stand for about 24 hours, it was found to contain a quantity of beautiful, large, well-defined, brilliant crystals. These were washed with a little cold water, and dried first on bibulous paper and then over sulphuric acid. They gave the following numbers on analysis :—

	I.	II.	III.	IV.
* Silver	39·27	39·39	39·35	39·28
Water	—	—	6·56	6·59

The water was determined by heating at 100° and also at 110°.

The formula C_4H_5,AgO_6,H_2O requires silver, 39·27; water, 6·54. Several preparations were made, and Professor Haushöfer was good enough to examine some of the crystals. The following are his results :—

Crystalline System, Monoclinic; a : b : c = 0·7205 : 1 : 0·8685; β = 70° 10′



Prismatic crystals usually developed in the direction of the orthopinacoïd. Crystals of the combinations $\infty\bar{P}\infty$ (100) = *a*, ∞P (·110) = *p*, 0P (001) = *c*, $\breve{P}\infty$ (011) = *q*, $\infty\breve{P}\infty$ (010) = *b*, $P\infty$ (10$\bar{1}$) = *r*. The surface *r* is wanting in most of the crystals. The surfaces *a* and *p* exhibit a fine vertical striation.

		Measured.	Calculated.	
a : *c* =	(100)(001) =	*109° 50′	— —	
p : *p* =	(110)(1$\bar{1}$0) =	*112 5	— —	(before)
q : *q* =	(011)(0$\bar{1}$1) =	*101 52	— —	(above)
q : *a* =	(011)(100) =	105 1	105° 16′	
q : *p* =	(011)(110) =	124 25	124 24	
r : *a* =	(10$\bar{1}$)(100) =	132 30	132 38	
q : *c* =	(011)(001) =	140 55	140 56	
b : *q* =	(010)(011) =	129 5	129 4	
b : *p* =	(010)(110) =	123 54	123 58	
a : *p* =	(100)(110) =	146 0	146 2	

This salt when heated with water becomes opaque, and is apparently converted into the ordinary silver tartrate, with separation of tartaric acid, which dissolves some of the salt. If boiled with a strong solution of tartaric acid, it dissolves, and on cooling a white product is first deposited, which afterwards changes into small crystals, consisting apparently of the above acid silver tartrate.

An acid silver racemate appears to be formed in the same way as the tartrates, but it is much less soluble in water, and the crystals are small. I have not been able to obtain it free from the neutral racemate. One specimen of this impure salt gave 45·3 per cent. of silver; this is much lower than the ordinary salt, which requires 59·3, and is good evidence that an acid racemate exists.

XXXVI.—*The Colouring Matter of* Drosera Whittakeri.

By Edward H. Rennie, M.A., D.Sc., Professor of Chemistry in the University of Adelaide, South Australia.

Preliminary Notice.

Among the many species of Drosera to be found in Australia, one, *Drosera Whittakeri*, which grows plentifully on the hills near Adelaide, is conspicuous in the spring-time by its pretty white flowers, resembling those of the white oxalis. This species is provided with a tuber, one apparently to each plant, which is found attached to a straight stem at a depth of 3 or 4 inches. These tubers invariably consist of an inner solid but soft nucleus, full of reddish sap or juice, and an outer series of easily detached thin and more or less dry layers of an almost black material. Between these layers is to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants. My attention was drawn to the plant by Professor Tate, of Adelaide University, and on inquiry I found that Mr. Francis, of this city, had extracted the colouring matter by means of carbon bisulphide, found that it was volatile, and that by its means beautiful tints could be produced on silk by the use of various mordants, but beyond that had not continued the investigation.

A preliminary examination having shown that the substance could be obtained in the crystalline condition, it was determined to further investigate it. The plant is easily obtainable in spring, but on the approach of summer the leaves dry up and disappear. When it is remembered that the yield of colouring matter is very small, that the tubers vary from ¼ to ¾ inch in diameter, and that to obtain each tuber it is necessary to dig down 4 or 5 inches, often in hard soil, it will be easily understood that a considerable amount of labour is required to collect even a moderate quantity. The time and labour at my disposal being limited, I have only been able to obtain about 4 quarts (weight unfortunately not noted) of the tubers. The crude colouring matter obtained, as described below, from this quantity did not amount to more than 5 or 6 grams at the utmost. The method of extraction was as follows:—

The tubers were well crushed, and repeatedly treated with hot strong alcohol, washed with strong alcohol till the filtrate became almost colourless, and the spirit then distilled off. The residue, still containing a little alcohol, was then mixed with some water, allowed to stand, and filtered. In this way, almost the whole of the colouring matter was obtained as a dark-red mass on the filter-paper. This was dried, and then sublimed. The subliming apparatus consisted of a common saucepan, over the mouth of which was placed an ordinary tinned-iron sand-bath dish, and then inverted over this a large glass funnel, having its neck closed by a cork. The filter-paper with the substance was placed on the tin dish, and the temperature raised till sublimation went on freely, but not to such a point as to cause fusion. A considerable amount of carbonaceous matter always remained behind, but this appeared to consist of a quantity of charred resinous (?) matter extracted by the alcohol, and not to be a product of decomposition, subsequent experiments having shown that sublimation of the purified material could be effected with little or no change.

The sublimate thus obtained was of a brilliant vermilion colour, partly adhering closely to the surface of the glass, and partly in feathery crystals. Three specimens of this apparently pure material were burnt with the following results:—

	I.	II.	III.
Carbon..........	62·00	61·35	62·46
Hydrogen........	4·27	4·84	4·51

These numbers being scarcely satisfactory for a homogeneous material, small quantities of the substance were dissolved in some suitable solvent, a few drops allowed to evaporate, and the residue examined microscopically. This at once revealed the presence of at least two substances, one crystallising in small reddish plates, and the other in longer yellow or reddish-yellow needles, the latter occurring chiefly on the *outer* rim of the evaporated drop, indicating later deposition and therefore greater solubility. After a few trials, it was found that one of these substances, being much less soluble, could be separated by crystallisation from boiling alcohol or boiling glacial acetic acid. From either of these liquids, the less soluble substance separates on cooling in small, brilliant, red plates, canoe-shaped under the microscope. Below are the results of combustion, the specimens used having been obtained from *different* portions of crude sublimate as follows:—

I. Crystallised three times from boiling glacial acetic acid.
II. No. I crystallised once more from the same solvent.
III. Crystallised first from glacial acetic acid, then twice from boiling alcohol, then twice more from glacial acetic acid.
IV. Crystallised first from boiling alcohol, then twice from glacial acetic acid.
V. Crystallised first from boiling alcohol, then three times from glacial acetic acid.

The crystallisation was in each case continued until a drop of the mother-liquid, evaporated on a glass slide, gave no further indication under the microscope of the presence of the reddish-yellow needles above alluded to.

	Substance.	CO_2.	H_2O.
I........	0·2109	0·4655	0·076
II........	0·2026	0·444	0·0715
III........	0·2116	0·4639	0·0764
IV........	0·2240	0·4895	0·0818
V........	0·2723	0·5974	0·0985

	Calculated for $C_{11}H_8O_5$.	Found. I.	II.	III.	IV.	V.
C	60·00	60·19	59·77	59·93	60·00	59·83
H*........	3·64	4·00	3·92	4·01	4·05	4·01
O	36·36	—	—	—	—	—
	100·00					

It is easily seen that the numbers agree fairly well with those required by the formula $C_{11}H_8O_5$, which may represent a *trihydroxymethylnaphthaquinone.* The reactions to be subsequently described seem to confirm this view.

The crystals are anhydrous, and when dry are magnificently brilliant in sunlight. All the specimens described above melted at or very near to 192—193°. The substance is soluble, although with some diffi-

---

[*] It was found afterwards that a slight defect in the drying apparatus was the probable cause of the rather high results for hydrogen.

culty, in boiling strong alcohol or glacial acetic acid, very sparingly soluble in the cold liquids, and almost completely precipitated by water, in which, however, it dissolves to a small extent on boiling. It dissolves more easily in ether, and less readily in benzene and carbon bisulphide. It is soluble in solutions of the caustic alkalis and ammonia, with production of a splendid deep violet-red colour, and is immediately precipitated by acids, or gradually by carbon dioxide. On mixing boiling dilute solutions of potash and this substance in strong alcohol, and cooling, a dark-coloured compound crystallised out, but the quantity obtained was too small to purify for analysis.

In order to get some proof of the nature of this material, attempts were made to discover the presence of hydroxyl-groups, but so far unsuccessfully—this, however, is probably due to the fact that want of material has prevented the repetition of experiments under proper conditions.

A small quantity of material heated with benzoic chloride at 180° in a sealed tube for several hours yielded only a tarry uninviting mass.

One gram of substance was heated with methyl alcohol, methyl iodide, and caustic potash in suitable proportions in a flask attached to a reflux condenser, but the resulting liquid, on acidification, yielded only the unchanged substance.

Oxidation.—The substance is easily and rapidly oxidised by nitric acid, chromic acid, alkaline permanganate or alkaline ferricyanide. In order to examine the products, one gram was heated in a flask (attached to reversed condenser) with a mixture of potassium dichromate and sulphuric acid containing about 5 per cent. of the former: carbon dioxide came off in abundance. As soon as action had ceased, the liquid was distilled nearly to dryness, the retort filled up with distilled water, the contents again distilled off, and this process repeated. The mixed distillates were neutralised with pure barium carbonate, filtered, evaporated in a platinum dish, the residue taken up in a small quantity of water, filtered, and again evaporated in a weighed dish and dried. The residue was crystalline, and answered to the qualitative tests for barium acetate.

Weight of barium acetate found = 0·602 gram = 0·2833 gram acetic acid = 28·33 per cent. Theoretically a *trihydroxymethylnaphthaquinone* should yield 27·27 per cent. of acetic acid on oxidation.

The salt gave on analysis 53 per cent. of barium instead of 53·72 per cent. as required by theory, so that it was not quite pure. This result, therefore, so far confirms the view expressed above as to the nature of the substance. Oxalic acid appears to be a product of oxidation by nitric acid, but this was not confirmed.

Reduction.—So far as preliminary experiments on a small scale in test-tubes are evidence, reduction is not easily effected by sodium amalgam, by zinc and hydrochloric acid, by iron and acetic acid, or by sulphurous acid. When, however, a boiling alcoholic (or acetic acid) solution is poured carefully into a boiling solution of stannous chloride in a mixture of alcohol (or acetic acid) with hydrochloric acid, the deep red colour of the solution rapidly passes into pale yellow, and on cooling a yellow substance crystallises out in brilliant scales, canoe-shaped under the microscope. Once or twice, when alcoholic solutions were used, the liquid on boiling for some time longer became green, and then violet-red; but as this change did not occur with acetic acid solutions, it was probably due to the formation of a small quantity of colouring matter caused by the alcohol or some contained impurity, especially as a specimen of substance which crystallised out green instead of yellow had the same melting point as the yellow material, and on recrystallisation from a mixture of alcohol and water regained its yellow colour. The crystals were filtered off, washed with water, and then dried in a vacuum over sulphuric acid. Two specimens thus prepared melted at 215—217°.

On combustion the following numbers were obtained:—

	Substance.	CO_2.	H_2O.
I.	0·2095	0·4558	0·093
II.	0·2183	0·4760	0·096

	Calculated for $C_{11}H_{10}O_5$.	Found.	
		I.	II.
C	59·46	59·33	59·42
H	4·50	4·93	4·88
O	36·04	—	—
	100·00		

The numbers, therefore, agree fairly well with those required for the corresponding hydroquinone. When dry, this substance is stable in the air, but if left in contact with alcohol or water it soon becomes red. This change, evidently due to reoxidation, is much more rapid in alkaline solution, especially on heating, when the deep violet-red colour characteristic of a solution of the original substance in alkali appears almost immediately. Oxidation occurs also when an attempt is made to sublime the reduced product in presence of air. It is easily soluble in alcohol and ether, less readily in benzene or carbon bisulphide.

Examination of the Mother-liquor after Separation of the first described Substance.—The mother-liquor, whether acetic or alcoholic, deposited on standing (in a covered beaker) a further small quantity of crystalline substance, which, however, proved to be the same as that already described.

On pouring off the clear liquid and adding water, a copious crystalline precipitate formed. This was filtered off, dried, and then boiled with ordinary strong acetic acid (not glacial) in such quantity as only to dissolve part of it, leaving perhaps about three-fourths undissolved, and the liquid filtered. The residue was then boiled again with the same solvent, this time in sufficient quantity to dissolve all but a very small portion, the latter filtered off and the liquid allowed to crystallise, and this operation then repeated, the object of the method of treatment being—first, to get rid of any more soluble matter; and, secondly, to remove any of the less soluble substance which might yet remain. The crystals thus obtained were *needles* quite different in appearance from the red plates above described, although to the eye of much the same colour. Under the microscope the single crystals seemed yellow, but wherever they overlapped the colour became deep orange to red, and the material was apparently homogeneous.

The quantity in hand was small, and did not allow of many recrystallisations to make sure of purity, but the melting point was fairly constant, several *different* specimens melting at 164—165°; one, however, melted at 170°. The numbers obtained on combustion agree fairly well among themselves and with those required for the formula $C_{11}H_8O_4$.

	Substance.	CO_2.	H_2O.
I........	0·2213	0·5194	0·0871
II........	0·2195	0·5136	0·0839
III........	0·2031	0·4780	0·0788

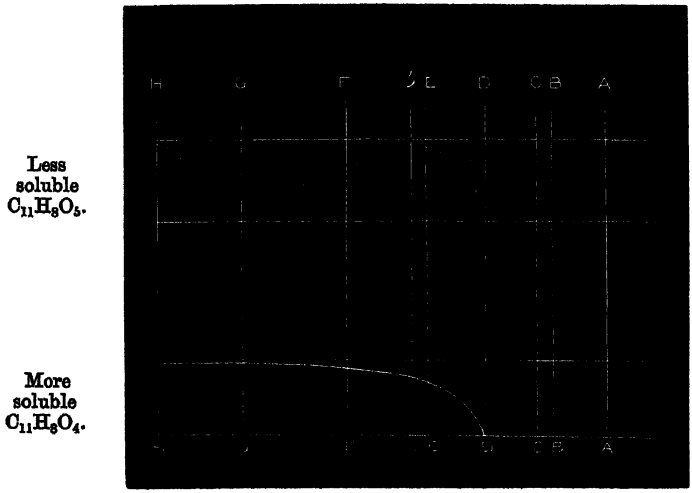
	Calculated for $C_{11}H_8O_4$.	Found.		
		I.	II.	III.
C	64·70	64·01	63·81	64·18
H	3·92	4·38	4·24	4·31
O	31·38	—	—	—
	100·00			

This substance is considerably more soluble than the other in all solvents tried. Its solution in caustic alkalis has simply a deep-red colour without any trace of violet, and this corresponds with a marked difference in the absorption spectrum as shown below.

Material was wanting for a study of the oxidation and reduction products in this case; but oxidation is readily effected as in the other case, and the deep-red solution becomes pale-yellow on treatment with stannous chloride as described above, but no crystals separate (at least in the experiment tried) indicating a much greater solubility of the reduced product.

In all probability, therefore, this second substance is also a derivative of methylnaphthaquinone, but contains one hydroxyl-group less than the first.

Absorption Spectra —The following are approximate representations of the absorption spectra of these two substances when dissolved in alcoholic potash, the upper dotted curve representing the less soluble substance $C_{11}H_8O_5$, whilst the lower represents the more soluble $C_{11}H_8O_4$.



Possibly there is still a third substance present, for the mother-liquor from the crystallisation of the second substance, when diluted, gives a precipitate, and this, when treated with boiling ordinary acetic acid, leaving a small quantity undissolved, yields a crop of crystals of lower melting point; if this process is repeated, the melting point becomes still lower. Whether this is due to some more soluble impurity which increases in proportion at each crystallisation, or to the presence of a third substance of lower melting point, I am at present unable to say, the quantity of material at my disposal being altogether insufficient.

There can be little doubt from the preliminary experiments that these colouring matters are derivatives of a methylnaphthaquinone. Possibly the red substance referred to at the outset as occurring between the outer layers of the tubers is the less soluble and more highly oxidised of the two, the soft juicy interior of the tubers containing the other, but this point must be left for further examination. I hope next spring to be able to secure a much larger quantity of material, and to follow up these results by a closer investigation.

XXXVII.—*Further Notes on the Di-Haloïd Derivatives of Thiocarbamide.*

By George McGowan, Ph.D., Demonstrator of Chemistry, University College of North Wales, Bangor.

Since the previous paper (Trans., 1886, 191), in which I described various dithiocarbamide-derivatives, I have continued the study of those compounds. This paper will be confined to the di-haloïd compounds of dithiocarbamide, leaving for future discussion some compounds of thiocarbamide with organic acid radicles.

Dithiocarbamide Dibromide, $(CSN_2H_4)_2Br_2$.

Claus (*Annalen*, **179**, 139) has already described dithiocarbamide dibromide, $(CSN_2H_4)_2Br_2$, obtained by the addition in molecular proportions of bromine to thiocarbamide, either in alcoholic, or with careful cooling, in aqueous solution; but he states at the same time that from the ease with which it decomposes, he found difficulty in getting it in a state sufficiently pure for analysis. I have, however, succeeded in obtaining it in beautiful large crystals, by the gradual addition of bromine to a moderately dilute aqueous solution of thiocarbamide, of course cooling whenever the solution tended to become too warm. On standing, the crystals are deposited, the substance not being very soluble in water. At the ordinary temperature the crystals are stable. A small portion of the substance (which had been dried on paper) was powdered, pressed between paper, and then placed over sulphuric acid in a vacuum.

0·1891 gram gave 28·0 c.c. N. at 14° C. and 779 mm.
Mercury pressure .... 17·99 per cent. N.
Calculated for $(CSN_2H_4)_2Br_2$. 17·95 „

Claus has already mentioned, that in outward appearance the dibromide is not to be distinguished from the dichloride, $(CSN_2H_4)_2Cl_2$. This is not only true for the needle-shaped crystals, as originally deposited from alcoholic solution, but also applies to their behaviour if dissolved in 90 per cent. alcohol on a microscopic slide, and allowed to recrystallise (already described by me for the dichloride, Trans., 1886, 191). Only, in the case of the dibromide, the plates deposited seem to be more elongated than in that of the chloride.

Action of Excess of Bromine on Thiocarbamide.

Another substance was formed, however, when the addition of bromine to the aqueous solution of thiocarbamide was continued, always with cooling, until it ceased to be absorbed, and the solution no longer gave a precipitate of sulphur on the addition of alkali, thus showing that dibromide was no longer present (Claus, *loc. cit.*). On nearly but not quite neutralising this solution with caustic potash, evaporating to dryness on a water-bath, and extracting the residue with boiling alcohol, the liquid deposited, after distilling off the alcohol, long, flat somewhat deliquescent prismatic crystals, mixed with cubes of potassium bromide. The former were freed from the potassium salt by a few recrystallisations from cold absolute alcohol, in which they are soluble, pressed between paper, and finally dried for a short time in the air-bath.

0·1255 gram gave 53·5 c.c. N at 8°, and 727·5 mm. mercury pressure = 49·27 per cent. N.

Calculated for carbamide, CON_2H_4, 46·66 per cent. N.

The melting point of these crystals was found to be 132—133° (not very sharp); carbamide fuses at 120°.

This result being unsatisfactory, a further quantity of the compound was prepared, but the product was found in this case to be very deliquescent and somewhat difficult to crystallise, owing, no doubt, to the presence of some cyanamide, and also to the fact that the amount at command was not very large; nitric acid was, therefore, added to its aqueous solution, when crystals of carbamide nitrate, CON_2H_4,HNO_3, were at once thrown down. These, after being redissolved in water and reprecipitated by nitric acid, were analysed.

0·1675 gram gave 48·6 c.c. N at 9°, and 741 mm. mercury pressure = 34·34 per cent. N.

Calculated for CON_2H_4,HNO_3 = 34·15 per cent. N.

This compound was, therefore, carbamide nitrate, and the original crystals were carbamide, CON_2H_4, not quite pure.

The residual salts, after the extraction of the whole mass by alcohol, were found to consist of bromide and sulphate of potassium, a portion of the latter having indeed already crystallised out from the aqueous solution before it was evaporated down.

The action of excess of bromine on thiocarbamide in aqueous solution, therefore, is to convert it into carbamide, or more probably in the first instance into cyanamide, thus:—

$$\underset{\text{Thiocarbamide.}}{CSN_2H_4} + 4Br_2 + 4H_2O = \underset{\text{Cyanamide.}}{CN{\cdot}NH_2} + 8HBr + H_2SO_4.$$

This is corroborated by the fact that 7·11 grams of nearly pure thiocarbamide required approximately 64 grams of bromine for oxidation, the calculated amount for the above equation being 60·0 grams.

The higher percentage of nitrogen found in the estimation at p. 379, viz., 49·27 per cent. instead of 46·66 per cent., was therefore no doubt due to the presence of a small quantity of dicyandiamide, polymerised from the cyanamide originally formed.

Action of Sulphuretted Hydrogen on Dithiocarbamide Dichloride, $(CSN_2H_4)_2Cl_2$.

If dithiocarbamide dichloride is dissolved in absolute alcohol, and sulphuretted hydrogen passed through the solution, sulphur is at once deposited.

(*a.*) 0·716 gram $(CSN_2H_4)_2Cl_2$ yielded 0·1015 gram S (washed and dried in air-bath).

Calculated for the equation—

$$(CSN_2H_4)_2Cl_2 + H_2S = S + 2CSN_2H_4,HCl,$$

we should have 0·1027 gram S.

The filtrate from the sulphur was evaporated over sulphuric acid in a vacuum, when some hydrochloric acid was given off, and crystals (well-formed four-sided pyramids) deposited. These were dried between paper for a chlorine determination.

0·2291 gram ignited with lime, gave 0·2249 gram AgCl = 24·3 per cent. Cl.

Calculated for CSN_2H_4,HCl = 31·56 per cent. Cl.

(*b.*) 0·922 gram $(CSN_2H_4)_2Cl_2$ yielded 0·1333 gram sulphur; calculated for the above equation 0·1323.

The alcoholic filtrate was evaporated exactly as above (it had an acid odour from hydrochloric acid), and the residual crystals were analysed.

0·1834 gram gave 0 1456 gram AgCl = 19·64 per cent. Cl.

Calculated for CSN_2H_4,HCl = 31·56 per cent. Cl.

The crystals contained no dichloride.

There can, therefore, be no doubt that the equation above given represents the action of sulphuretted hydrogen on dithiocarbamide dichloride in alcoholic solution. But the thiocarbamide hydrochloride, CSN_2H_4,HCl, formed, not being very stable, is partly decomposed into thiocarbamide and hydrochloric acid.

Action of Cyanides on Thiocarbamide and its Dichloride.

I have made a good many attempts to prepare what would be a highly interesting compound, viz., dithiocarbamide dicyanide, but without success. I may, however, here shortly describe the action of a few cyanides on thiocarbamide and its dichloride.

(1.) *Cyanogen Iodide*, ICN.—If iodide of cyanogen is dissolved in absolute ether, an equivalent quantity of finely-powdered thiocarbamide added, and the whole shaken up, the thiocarbamide—itself insoluble in ether—dissolves completely, while the liquid becomes dark from separated iodine; possibly the following reaction occurs, at least in the first instance:—

$$2CSN_2H_4 + 2ICN = (CSN_2H_4)_2(CN)_2 + I_2.$$

On shaking up this ethereal solution with excess of mercury, in the hope of getting rid of the iodine, a yellow-coloured solution was obtained, which, on evaporation of the ether, left a viscid orange-coloured mass, smelling of hydrocyanic acid. On dissolving this in a little alcohol, and then adding excess of water, a white milky precipitate was formed, which agglomerated immediately to a yellow mass. This was collected and dried, first over sulphuric acid, and finally at a temperature of about 50°.

0·1301 gram gave 6·05 c.c. N at 11° 1747 mm. mercury pressure = 5·45 per cent. N.

This substance was found to contain both iodine and mercury, and is therefore nothing else than the double compound of thiocarbamide with mercuric iodide, CSN_2H_4,HgI_2, already described by Maly (*Ber.*, **9**, 173), which contains 5·29 per cent. N. It crystallises from alcohol in radiating groups of needles.

(2.) *Silver Cyanide*, AgCN. — If dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$, dissolved either in a little water or alcohol, or without any solvent whatever, is rubbed in a mortar with cyanide of silver, hydrocyanic acid escapes, and the solution is found to contain thiocyanate, and, on slow evaporation, deposits crystals of ammonium chloride. This evolution of hydrocyanic acid takes place even if the two compounds, just moistened with absolute alcohol, are allowed to react on each other in a vessel surrounded by a mixture of ice and salt.

(3.) *Potassium Cyanide*, KCN.—The action here is very similar to that of silver cyanide. If a little dithiocarbamide dichloride is added to a cold aqueous solution of potassium cyanide, it dissolves, hydrocyanic acid being evolved. If the dichloride, in alcoholic solution, is heated with excess of finely powdered cyanide of potassium, much ammonia and hydrocyanic acid are given off, while the resulting liquid is found to contain thiocarbamide,* and a small quantity of a brownish liquid with an aromatic odour.

---

* The amount got was necessarily very small. On analysis, it yielded 38·7 per cent. N; calculated for CSN_2H_4 36 85 per cent. Besides this, its general appearance and behaviour corresponded exactly with that of thiocarbamide.

(4.) *Silver Potassium Cyanide*, AgCN,KCN.—0·318 gram of this double cyanide (2 mols.) and 0·178 gram dithiocarbamide dichloride (1 mol.) were dissolved in water separately, and the solutions mixed, when a precipitate of silver cyanide at once came down. The filtrate from this was strongly acid to test-papers, and smelt of hydrocyanic acid. It contained no unchanged dichloride, and no ammonium salt, but much thiocyanate.

In order to determine the quantity of hydrocyanic acid evolved in the above reaction, 0·5 gram (that is, an excess) of the double cyanide of silver and potassium was added to an aqueous solution of 0·234 gram dichloride in a flask, which was then heated till no more hydrocyanic acid was given off; the vapours were passed into a solution of nitrate of silver acidified with nitric acid, and the resulting silver cyanide was finally converted into chloride. In this way, 0·2695 gram of AgCl were obtained, corresponding with 0·0507 gram HCN evolved. Now, according to the following equation—

$$(CSN_2H_4)_2Cl_2 + 2AgCN,KCN = CSN_2H_4 + CNNH_2 + S + 2HCN + 2KCl + 2AgCN,$$

there ought to be 0·0547 gram HCN, which agrees very closely with the result got.

This reaction, and those with the other cyanides, point therefore to the formation, in the first instance, of dithiocarbamide dicyanide, which immediately decomposes, probably in the same way as the other di-haloïd compounds of thiocarbamide do when their solutions are heated, or on addition of an alkali, or simply on standing (Claus, *loc. cit.*), the sulphur which is liberated being, however, in this case taken up by the excess of cyanide present, with the formation of thiocyanate.

University College of N. Wales, Bangor,
February, 1887.

XXXVIII.—*Researches on Chrom-organic Acids.*

By Emil A. Werner, Assistant in the Chemical Laboratory, University of Dublin.

When oxalic acid is used to reduce potassium dichromate, two distinct compounds can be obtained according to the conditions under which the experiment is performed.

1st. If the oxalic acid is in large excess, and partly present as acid potassium salt, the beautiful "blue oxalate of chromium and potassium" is obtained, discovered by Dr. Gregory in 1837.

2nd. If the oxalic acid used for reduction be not in very great excess, and none of it as the potassium salt, a fine red salt will be formed which was discovered by Crofts in 1842.

The compounds thus obtained have been generally treated as "double salts," that is, as molecular compounds of chromium oxalate with oxalate of potassium, or any of the other metals which can be made to displace potassium in those compounds. Malaguti, however, took a different view of their nature, and pointed out (*Compt. rend.*, **16**, 456) that "the oxide of chromium, and probably all the oxides of the same formula, can, in combining with certain organic acids, give rise to compounds which, far from being salts, are veritable acids." Malaguti's view seems to have attracted little attention, as it has been almost ignored by other chemists (with the exception of Clarke and Kebler) who have worked with these remarkable chromium-derivatives.

My examination of these substances has led me to the conclusion that they are salts of complex chromoxalic acids, and that other organic acids can be more or less completely substituted for oxalic acid in some of these compounds.

In the present paper, I propose to describe the results obtained with salts of chromoxalic acid, and primarily to show that the formula of Gregory's salt, $K_3Cr(C_2O_4)_3,3H_2O$, must be doubled.

Part I.

On certain Chromoxalates (Blue Series).

A quantity of Gregory's salt was prepared according to its discoverer's directions, and analysed with the results stated below The method adopted for the analysis of this salt and of the different compounds described, was as follows: the substance was ignited in a platinum crucible with free access of air, the residue consisting of a mixture of potassic chromate and carbonate was dissolved in water, the acidified solution reduced by boiling with alcohol, and the chromium precipitated with ammonia; the potassium was estimated in the filtrate by evaporating to dryness, igniting, and weighing as sulphate. The oxalic radicle was estimated by boiling the aqueous solution of the salt with a slight excess of potash until completely decomposed, filtering from precipitated chromic hydrate, and determining the oxalic acid in the filtrate, after acidifying with sulphuric acid, by means of potassium permanganate.

	Theory.		Found. I.	Found. II.
K_6........	24·02	per cent.	23·84	—
Cr_2.......	10·68	„	11·08	11·14
$(C_2O_4)_6$....	54·20	„	53·84	53·09
$(H_2O)_6$....	11·10	„	11·24 (by diff.)	—
	100·00		100·00	

The formation of this salt is represented by the following equation:—

$$K_2Cr_2O_7 + 4KHC_2O_4 + 5H_2C_2O_4 = K_6Cr_2(C_2O_4)_6 + 6CO_2 + 7H_2O;$$

and its decomposition on ignition as—

$$K_6Cr_2(C_2O_4)_6 + 9O = 2K_2CrO_4 + K_2CO_3 + 11CO_2,$$

which requires a residue amounting to 54 per cent. of the crystallised salt; 1·424 gram ignited with free access of air left a residue weighing 0·7645 gram, equal to 53·69 per cent. of the original weight.

The proof that the doubled formula used above is the correct one is afforded by the formation of the well-defined compound $K_5(NH_4)Cr_2(C_2O_4)_6,6H_2O$, which is obtained by replacing one molecule of KHC_2O_4 by $(NH_4)HC_2O_4$ in the equation representing the formation of Gregory's salt. The ammonium in this compound was determined by distillation with soda solution, using an apparatus somewhat similar to that described by Holmes (*Chem. News*, 52, 49)—

	Theory.		Found. I.	Found. II.
K_5........	20·47	per cent.	21·14	21·17
NH_4......	1·88	„	1·75	1·88
Cr_2.......	10·92	„	11·40	10·91
$(C_2O_4)_6$....	55·40	„	55·61	55·40
$(H_2O)_6$....	11·33	„	11·10 (by diff.)	11·33
	100·00		100·00	

This compound crystallises in deep-blue rhombic prisms, indistinguishable in appearance from Gregory's compound, and possessing similar properties. 0·7663 gram ignited left a residue weighing 0·3728 gram = 48·70 per cent., consisting of chromate and carbonate of potassium. The decomposition is represented by the following equation:—

$$2K_5(NH_4)Cr_2(C_2O_4)_6 + 9O_2 = 4K_2CrO_4 + K_2CO_3 + 2NH_3 + 23CO_2 + H_2O,$$

which requires a residue amounting to 47·95 per cent. of the crystalline salt.

The decomposition of these salts on ignition is given as being characteristic, and furnishing at the same time corroborative evidence of the formula of the particular compound.

I may mention here a salt prepared by replacing the KHC_2O_4 by $NaHC_2O_4$; the resulting compound, which is exceedingly soluble in water, and crystallises very imperfectly, has the formula

$$K_2Na_4Cr_2(C_2O_4)_6,8H_2O,$$

as deduced from the following analysis:—

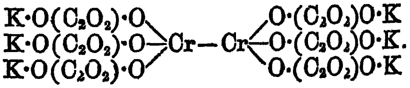
	Theory.		Found. I.	Found. II.
K_2	8·24	per cent.	8·09	—
Na_4	9·72	„	9·37	—
Cr_2	10·99	„	11·37	—
$(C_2O_4)_6$	55·84	„	56·18	56·12
$(H_2O)_8$	15·21	„	14·91	—
	100·00		99·92	

When ignited under the same conditions as the other salts, this compound, unlike them, leaves a readily fusible residue: 0·6555 gram left residue weighing 0·3162 gram, equal to 48·23 per cent. The decomposition of the salt is represented by the equation—

$$K_2Na_4Cr_2(C_2O_4)_6,8H_2O + 9O = 2Na_2CrO_4 + K_2CO_3 + 11CO_2 + 8H_2O,$$

which requires a residue amounting to 48·83 per cent.

The fact of chief importance connected with these salts is that their solutions are not precipitated by calcium chloride or ammonia: moreover, when they are treated with solutions of certain of the heavier metals, as lead, silver, barium, &c., they do not yield simple oxalates by double decomposition, but salts which contain the new metal in the place previously occupied by the alkali metal. These facts suggest a more intimate union between the chromium and oxalic groups, than that which is usually supposed to exist in what are commonly accepted as double salts; in other words, it appears that in these compounds the group $Cr_2(C_2O_4)_6$ plays the part of an acid radicle, giving rise to a complex chrom-organic acid of which Gregory's blue compound is the normal potassium salt, viz., potassium chromoxalate; the acid itself being hexabasic. On this view, I propose to represent the constitution of the salt thus:—



$$\begin{matrix} K\cdot O(C_2O_2)\cdot O \\ K\cdot O(C_2O_2)\cdot O \\ K\cdot O(C_2O_2)\cdot O \end{matrix} \Big> Cr - Cr \Big< \begin{matrix} O\cdot(C_2O_2)O\cdot K \\ O\cdot(C_2O_2)O\cdot K. \\ O\cdot(C_2O_2)O\cdot K \end{matrix}$$

On referring to the literature of the subject, I found, as already stated, that a somewhat similar hypothesis had been advanced by Malaguti in 1843 in a letter to Dumas (*Compt. rend.*, **16**, 456); the statement concerning the constitution of these compounds, which I have given in his own words at the commencement of this paper, is, however, disputed by Löwel (*Compt. rend.*, **16**, 862). He considers them to be double and triple salts, as does Rees Reece (*Compt. rend.*, **21**, 1116), who prepared a number of similar salts by double decomposition, besides analogous compounds containing iron and aluminium.

When we examine the salts containing other metals, it soon becomes evident that the alkali metals occupy a position in these compounds quite distinct from that of the chromium.

Hartley's (*Proc. Roy. Soc.*, **21**, 499) calcium compound,

$$KCaCr(C_2O_4)_3,4H_2O,$$

termed by him "potassio-calcic chromic oxalate," was prepared according to his directions. I experienced some difficulty at first in obtaining this compound free from calcic oxalate, but by filtering a hot concentrated solution into a vessel immersed in a freezing mixture, small, but well-defined, perfectly pure crystals were obtained. After drying by pressure, and for a short time over oil of vitriol, these gave on analysis results agreeing with those obtained by Hartley, but his formula must now be doubled:—

	Theory.		Found.	
			I.	II.
K_2	8·36 per cent.		8·71	—
Ca_2	8·56	„	8·43	8·68
Cr_2	11·14	„	11·42	—
$(C_2O_4)_6$....	56:53	„	57·04	56·88
$(H_2O)_8$....	15·41	„	13·89	—
	100·00		99·49	

The water determination in the above analysis is low, from the fact that it is impossible to obtain this salt free from moisture without its parting with a small portion of water of crystallisation, which it loses very readily over oil of vitriol.

In an experiment, with a view to prepare a further quantity of this salt, *cold* moderately dilute solutions of calcium chloride and the blue potash salt were mixed (Hartley recommends warm dilute solutions); the liquid was allowed to stand for a few days in a large flask, and at the end of that time a quantity of crystals had deposited, in tufts of prismatic needles; these when dried were of a fine deep-blue colour, much larger than Hartley's salt, and entirely devoid of the beautiful greenish lustre so characteristic of the latter. On analysis, this compound gave results agreeing with the formula $K_2Ca_2Cr_2(C_2O_4)_6,6H_2O$, differing therefore from Hartley's salt by 2 mols. of water of crystallisation:—

			Found.	
	Theory.		I.	II.
K_2........	8·68	per cent.	9·14	—
Ca_2	8·90	,,	8·94	8·85
Cr_2	11·58	,,	10·84	—
$(C_2O_4)_6$ ...	58·79	,,	58·68	58·79
$(H_2O)_6$....	12·05	,,	11·75	
	100·00		99·35	

The mother-liquor from these crystals furnished a quantity of Hartley's salt. I have since made unsuccessful attempts to obtain a further quantity of this hexa-hydrated compound; its formation appears to be entirely dependent on the degree of concentration of the mixed solutions. These two calcium salts, differing from each other in their composition by only 2 mols. H_2O, possess very different physical properties, as seen from the following table:—

1. Formula— $K_2Ca_2Cr_2(C_2O_4)_6 \cdot 8H_2O$.	Minute crystalline needles possessing a beautiful greenish lustre.	Partially decomposed by hot water, with separation of calcic oxalate.
2. Formula— $K_2Ca_2Cr_2(C_2O_4)_6 \cdot 6H_2O$.	Prismatic needles, black by reflected light, blue by transmitted light.	Not evidently decomposed by water.

These salts containing calcium in combination with the oxalic radicle to the extent of over half the weight of the entire compound, are soluble in water, yet the addition of a soluble oxalate immediately precipitates the calcium; this behaviour furnishes, I think, a striking proof that these compounds are not double salts. An attempt to prepare a salt containing calcium only, by mixing an excess of calcium chloride with the blue salt, was unsuccessful, no definite compound separating from the concentrated solution. The corresponding barium salt, which is very characteristic, is readily obtained by precipitating the blue salt with an excess of barium chloride.

This compound crystallises in fine, long, silky needles, of a pale greenish colour, slightly dichroic; sparingly soluble in cold, readily soluble in hot water, a tolerably concentrated solution gelatinises on cooling. The composition of this salt is $Ba_3Cr_2(C_2O_4)_6,8H_2O$:—

	Theory.		Found.	
			I.	II.
Ba_3	34·62 per cent.		34·48	34·53
Cr_2	8·70	„	8·47	—
$(C_2O_4)_6$	44·49	„	44·29	—
$(H_2O)_8$	12·19	„	12·26	—
	100 00		99·50	

When ignited, this salt leaves a residue of barium chromate and carbonate, the decomposition being—

$$Ba_3Cr_2(C_2O_4)_6 + 9O = 2BaCrO_4 + BaCO_3 + 11CO_2.$$

Two tribaric salts, containing respectively 12 and 18 mols. of water of crystallisation, are described by Rees Reece (*Compt. rend.*, **21**, 1116), while Clarke (*Ber.*, **14**, 36) describes one containing 7 mols. H_2O, the existence of which is doubtful, as it seems a peculiar property of all these salts to crystallise with an even number of water molecules.

By treating the barium salt with dilute sulphuric acid, the barium is precipitated, and a liquid is obtained possessing a deep greenish-red colour, strongly dichroic, not precipitated by excess of ammonia, nor by calcium chloride; treated with potash (not in excess) it yields the original blue salt on evaporation. This liquid in all probability contains the acid $H_6Cr_2(C_2O_4)_6$ in solution, which, however, I have not yet succeeded in isolating, as the liquid decomposes on evaporation even in a vacuum, with separation of oxalic acid. A similar solution is obtained by acting on oxalic acid with a solution of chromic acid in proportions represented by the equation—

$$H_2Cr_2O_7 + 9H_2C_2O_4 = H_6Cr_2(C_2O_4)_6 + 7H_2O + 6CO_2.$$

On attempting to throw the compound down by the addition of strong alcohol to the aqueous solution, it was found that it mixed readily with the latter, the compound being therefore soluble in alcohol. A quantity of the barium salt in fine powder was suspended in absolute alcohol, and decomposed by the calculated quantity of sulphuric acid; the complete decomposition of the barium salt in presence of the strong alcohol takes several hours, being very slow even at the boiling point of the alcohol. The mixture was allowed to stand several days, and the resulting deep greenish-red alcoholic solution filtered from the barium sulphate. On concentration, the solution refused to crystallise, but when evaporated to dryness, it left a bright green amorphous residue, exceedingly deliquescent, and possessing a peculiar ethereal odour. When ignited, this compound leaves a residue of chromic oxide, amounting to 17·48 per cent. of the original weight; for want of material it has not yet been investigated or analysed, suffice it to say here that it is not the acid $H_6Cr_2(C_2O_4)_6$, but appears to be an ethereal compound, as when treated with water it is decomposed with separation of a heavy oily liquid (ethylic oxalate?). I hope later on to fully investigate this peculiar compound, and give the results in a future communication. I have also obtained other salts of the blue series by the addition of certain oxalates to the red series; these include compounds containing various organic bases, as aniline, carbamide, &c., &c., and will be described in a future paper.

University Laboratory,
Trinity College, Dublin.

XXXIX.—*Supersaturation of Salt Solutions.*

By W. W. J. Nicol, M.A., D.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham.

In previous papers on this subject (*Phil. Mag.*, 1885, June and September), I brought forward the view formerly advanced by Loewel (*Ann. Chim. Phys.* [3], 49—51), that solutions usually regarded as supersaturated are not really so, but owe their formation to the fact that the salt dissolved is not the same as that which crystallises out in the solid state. Considerable support is given to this view by the fact that the salts which exhibit the property of forming supersaturated solutions are all hydrated when crystallised from solution at the ordinary temperature, no well authenticated instance existing, so far as I am aware, of supersaturation of a solution of a salt which crystallises without water.* While on the other hand, if the solutions of anhydrous salts are examined at low temperatures, temperatures at which hydrates are formed, then supersaturation is readily produced (Guthrie, *Phil. Mag.* [4], **49**, 1).

---

* Gmelin (*Handbook*, vol. i, page 11), it is true, states that potassium dichro-

Supersaturation has been frequently compared to superfusion, the analogy being suggested by the usual method of preparing supersaturated solutions by cooling hot solutions, but it has been shown by de Coppet (*Compt. rend.*, 1871, **73**, 1324) and myself (*loc. cit.*) that supersaturated solutions can be readily prepared by dissolving cold dehydrated salt in cold water, and I have shown (*loc. cit.*) that such solutions are identical, so far as amount of dissolved salt is concerned, with solutions prepared by the aid of heat. Thus the analogy breaks down; in addition, supersaturated solutions are perfectly stable; so long as air is excluded, they may be shaken, either alone or with sharp particles such as broken glass; a current sufficiently strong to decompose the water is without effect on them, and finally they may be frozen without formation of the hydrate, which is at once produced by the addition of a crystal of the solid salt. In fact, the sole cause, which *never* fails to terminate the state of supersaturation, is contact with a crystal of the hydrate, or of a salt isomorphous with it.

In the papers referred to, I ascribed the formation of supersaturated solutions to the existence in solution of what may, for want of a better term, be called the anhydrous salt. According to this view, supersaturated solutions differ in no way from ordinary solutions, they are merely saturated or non-saturated solutions of the anhydrous salt, combination with water to form the hydrate taking place only at the moment of crystallisation. These views have met with but little acceptance, however, by those who are interested in the subject, the colour of some dissolved salts being regarded as positive proof of the existence of the hydrate in solution, moreover, stress has been laid on the fact that the experiments were made in one case with sodium sulphate, which is regarded as an exceptional salt; but on the other hand, these experiments were borne out by others on sodium thiosulphate, which exhibits no apparently exceptional behaviour in its solubility.

In order to bring more experimental evidence to bear on this difficult problem, I venture to lay the results of further experiments before the Society. These naturally fall into two groups.

---

mate and silver nitrate are exceptions to the above; and F. Kohlrausch (*Ann Phys. Chem.*, **6**, 28) claims to have prepared a supersaturated solution of ammonium chloride, while elsewhere I have seen it stated that potassium nitrate exhibits this property. I have myself attempted in vain to prepare supersaturated solutions of anhydrous salts; and Dr. Tilden informs me that he also has been uniformly unsuccessful.

1. Experiments showing that ordinary and supersaturated solutions of the same salt have the same constitution; and

2. Those which show that solutions of a salt do not contain the hydrate which is known in the solid state.

The first of these cases can be approached from two sides. It is possible to pass from an ordinary solution to a supersaturated one, either by lowering the temperature of a solution containing a definite amount of salt, or by increasing the amount of salt dissolved at a definite temperature. Each of these methods yields evidence which is only partially conclusive, but the two together make the proof complete.

Amount of Salt Constant, Temperature Falling.

A solution of a salt saturated at any one temperature is supersaturated when the temperature falls, and non-saturated if it rises. With such a solution 10° or more above its saturation temperature, it will be possible by examination of the curves representing the various physical constants as the temperature falls to ascertain whether these exhibit any change in direction, gradual it may be, but still decided, in passing the saturation temperature.

Taking the various physical constants, so far as they have been determined in this connection, we have first the electric conductivity, as examined by Heim, the results of whose experiments have been recently published (*Ann. Ph. Chem.*, 1886, 27, 643). His observations were made with solutions of the salts, zinc sulphate, sodium sulphate, magnesium sulphate, sodium carbonate, and calcium chloride, and are thus fairly representative of the various hydrated salts which form supersaturated solutions. The method of experimenting was that indicated above; a solution of the salt under examination was prepared saturated at some intermediate temperature, such as 30°; it was then heated to 60°, and the specific resistance was determined at every few degrees as the temperature fell to 10°, or even lower. The results are summed up by Heim, as follows:—

"The published experimental figures and the curves representing these clearly show that none of the salt solutions examined exhibit any sudden change in their specific resistance, as they pass into the supersaturated condition. . . . . It is not possible, by the mere inspection of the curves, to determine whether or from what point the solution was supersaturated."

Heim believes that this is proof of Loewel's view that a solution contains the anhydrous salt, and that there are no truly supersaturated solutions. In this I believe he is mistaken; his results furnish proof that the constitution of a solution is not altered in passing from the nonsaturated to the supersaturated condition by fall of temperature; this is only one half of the proof.

Secondly, we have the specific viscosity as a means of examining this subject. I have made experiments on solutions of sodium sulphate, phosphate, and carbonate, saturated at about 30°. The form of apparatus employed and the precautions taken will be described in a future communication on the specific viscosity of salt solutions. The principle was the same as that of Heim. The results are contained in Table I, where the strength, saturation temperature, and the specific viscosity are given, the last being the time of flow of the salt solution, multiplied by 100, and divided by the time of flow of pure water at 20°. The temperatures of observations were 20°, 25°, 30°, 35°, 40°, and in the case of the sodium sulphate solution every degree between 30° and 35°. The curves corresponding to the results are shown in Plate I, a vertical dotted line indicating the saturation temperature. In this case also the curve is perfectly continuous; there is nothing to indicate any change in the constitution of the solution.

TABLE I.

$t°$.	Na_2SO_4.	$t°$.	$Na_2S_2O_3$.	$t°$.	Na_2HPO_4.
20·0°	459·4	20°	834·4	20°	405·4
24·9	388·2	25	685·2	25	340 4
30·0	332·9	30	574·5	30	291 3
31·1	322·9	—	—	—	—
32·2	313·2	—	—	—	—
33·2	304·6	—	—	—	—
34·2	297·1	—	—	—	—
35·1	289·8	35·1	487·1	35	251·3
40·0	254·2	40·0	420·7	40	220·3
Strength	45/100	79/100		26/100	
Saturation $t°$	31·2°	28°		31°	

Thirdly, there is the rate of expansion of supersaturated solutions. This I determined only qualitatively in the following way:—A solution of the salt saturated at about 30° was placed in a bulb furnished with a hollow stopper, to which was attached a long glass tube of uniform bore, graduated in millimetres. This last was surrounded by a glass jacket, through which water from the main flowed in a constant stream. The solution, nearly filling the bulb, was covered with a layer of paraffin oil, and the stopper inserted. The bulb was then placed in a bath, side by side with a thermometer divided into tenths, the approximate ratio of the contents of each mm. of the tube to the contents of the bulb was 1·5 : 100,000. No attempt was made to take account of the amount of paraffin present, as the experiments were intended solely to ascertain whether the expansion between 20° and 40° was uniform or not. I therefore give only the curves corresponding to the results, as read in mm. of the tube. Salts were examined of the following concentration and saturation temperature:—

Salt.	x/100.	Sat t°.
Sodium sulphate............	44/100	30
Zinc sulphate	64/100	30
Sodium carbonate	38/100	30
Magnesium sulphate	41/100	30

The solubility of these at 20° and 40° being—

Salt.	20°.	40°.
Sodium sulphate	19·5/100	48·8/100
Zinc sulphate..............	57/100	72/100
Sodium carbonate..........	21·4/100	46·2/100
Magnesium sulphate........	36·2/100	45·6/100

Here, again, it is impossible to detect the saturation temperature by mere inspection of the volume curves (Plate II).

These experiments on the various physical constants prove completely that there is no change in the constitution of the solution in passing the saturation point. In other words, that a supersaturated solution has the same constitution as a saturated solution prepared in the same way. It remains to be proved that it is the same as that of a non-saturated solution prepared in the ordinary way.

Temperature Constant, Concentration Varying.

In this connection I can bring forward determinations of only two physical constants, density and specific viscosity. The results obtained by experiment on the densities of solutions of sodium sulphate and thiosulphate are contained in a previous paper (*loc. cit.*). But I introduce the curves here (Plate II) for the sake of completeness. It will be seen that the density curve is perfectly regular in the case of both salts, nothing indicates supersaturation. It must be remembered that determinations of the density of supersaturated solutions are liable to greater experimental error than ordinary determinations; loss of water is almost unavoidable in the preparation of such solutions, and twice the usual error is introduced, owing to the necessity for employing a liquid to protect the solution. Similar results were also obtained by Schiff, so that it is certain that the density curves do not change their direction at the saturation point.

Secondly, the specific viscosity at constant temperature increases uniformly with uniform increase of dissolved salt. This is shown by the results in Table II. Experiments were made with sodium sulphate, carbonate, and phosphate, and the solutions were of such strength that they extended equal distances on either side of the saturation point. The amounts of salt are in parts per 100 of water, not percentages.* Plate III gives the corresponding curves, which are again perfectly uniform and continuous on either side of the saturation point.

TABLE II.

x/100.	Na_2SO_4.	x/100.	Na_2HPO_4.	x/100.	Na_2CO_3.
10·0	134·7	5·0	124·2	10·0	165·3
12·5	146·0	7·5	139·2	12·5	189·4
15·0	158·8	10·0†	156·6	15·0	219·2
17·5	173·1	12·5	178·2	17·5	253·4
20·0†	188·4	15·0	205·6	20·0†	292·9
22·5	205·7	—	—	22·5	342·3
25·0	224·2	—	—	25·0	401·2
27·5	245·5	—	—	27·5	466·3
30·0	268·4	—	—	30·0	546·3

These experiments show that supersaturated solutions have the same constitution as non-saturated solutions at the same temperature, and those in the first part of the paper proved that alteration of temperature produces no abrupt change when the solution passes from the one state to the other. There can thus be no doubt that dilute, saturated, and supersaturated solutions all have the same constitution. This being the case, supersaturation cannot be explained by the hypothesis that the state of hydration of the dissolved salt is different in the two cases, nor can we fall back on the "inertia" of Kremers, for I have shown that a supersaturated solution can dissolve dehydrated salt. Some other explanation must therefore be sought for. This is to be found, I believe, in the statements in my previous paper.

"The individual in solution is not the same as that in the solid state, when hydrated salts are considered.

"A supersaturated solution is a solution of the anhydrous salt, which may or may not be saturated."

---

* The solutions were prepared by dissolving weighed quantities of salt in *measured* quantities of water, and are thus only approximate.

† Nearly saturated.

There is a good deal of evidence in support of the former of these statements, thus:—

Loewel (*Ann. Chim. Phys* [3], **49**, 32) found that a supersaturated solution of sodium sulphate deposited either the heptahydrate or decahydrate, according to which hydrate was used to terminate supersaturation, and he obtained similar results with other salts, such as sodium carbonate, magnesium sulphate.

Again, it has been found that a supersaturated solution of nickel sulphate deposits the pentahydrate or heptahydrate under similar conditions, while Gernez (*Compt. rend.*, 1867, **63**, 843) found that supersaturated solutions of the salts of racemic acid deposited dextro- or lævo-tartrate, according to which crystal was introduced into the solution.

Now it does not seem probable that were the salt in solution combined with its maximum amount of water of hydration, that mere contact with a crystal of lower hydration could effect the separation of two or three or more molecules of water, more especially in presence of excess of water. But in addition I am able to bring forward evidence, in one case at least, which proves that the individual in solution is not the same as that in the solid state. In my previous paper I described the formation of crystals in a supersaturated solution of sodium thiosulphate which had been prepared several years before, by fusion of the solid salt, and probably by boiling before sealing the tube; of this last I am not certain. These crystals contained less than 2 mols. H_2O, though they were only partially separated from the mother-liquor. This led me to try evaporation of a supersaturated solution at the ordinary temperature over sulphuric acid, and as sodium thiosulphate forms very stable supersaturated solutions, I fused some crystals, and exposed the solution over sulphuric acid for two days, at a temperature between 16° and 21°, with the result that an abundant crop of crystals was obtained. On decanting the mother-liquor into a dish, it immediately solidified, and the crystals were again exposed over sulphuric acid for 24 hours; at the end of that time they were surface-dry, were perfectly transparent, and not effloresced in the least, showing that they were in the same state of hydration as when deposited from the solution. When, however, they were touched they crackled, grew warm, and slightly opaque. On heating they liquefied partially, and a liquid was obtained which contained solid transparent crystals; this showing that the substance contained mother-liquor, which had crystallised as pentahydrate. Two analyses of the crystals gave 15·6 per cent. of water, corresponding with 1·6 mol. H_2O to 1 mol. of the anhydrous salt. Thus the crystals produced by the evaporation of a supersaturated solution of sodium thiosulphate have at the most the formula

$(Na_2S_2O_3)_2,3H_2O$, or more probably $Na_2S_2O_3,H_2O$, the latter formula indicating the presence of about 25 per cent. of the pentahydrate. In any case, the results show that the salt deposited from the supersaturated solution is not the pentahydrate, and that consequently the pentahydrate is not present in the solution. I hope soon to be able to describe the results of similar experiments with other salts. But what I have said, taken in conjunction with the experiments formerly described, when I prepared supersaturated solutions by dissolving cold salt in cold water, or in cold non-saturated solutions of the same salt, put it beyond question that such solutions do not contain the hydrate which exists in the solid state.

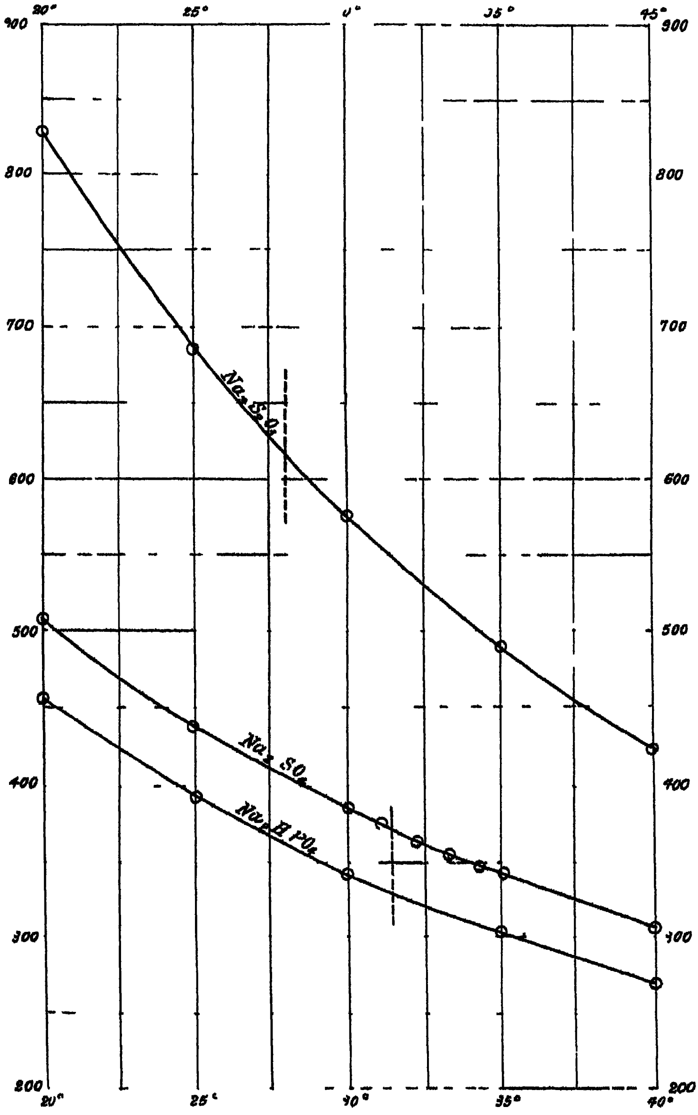
The second statement that supersaturated solutions are saturated or non-saturated solutions of the *anhydrous* salt is not so easily proved. It must stand or fall with the hypothesis that all solutions contain the *anhydrous* salt, and I must emphasise here once more that by this I do not mean anhydrous in the sense when applied to a solid salt, but as opposed to the view that any portion of the water is connected with the salt in a way different from the rest of the water.

This homogeneity, so to speak, of the solvent water is so clearly proved by experiments on vapour-pressures, freezing points, molecular volumes, electric conductivity, and other physical constants of solutions, that I think we ought to hesitate before asserting that hydrates exist in solution, the sole evidence in the support of this being heat evolved on solution of dehydrated salts as opposed to the absorption of heat attending the solution of the hydrates, and the colour-changes attending the warming or other treatment of solutions of certain salts.

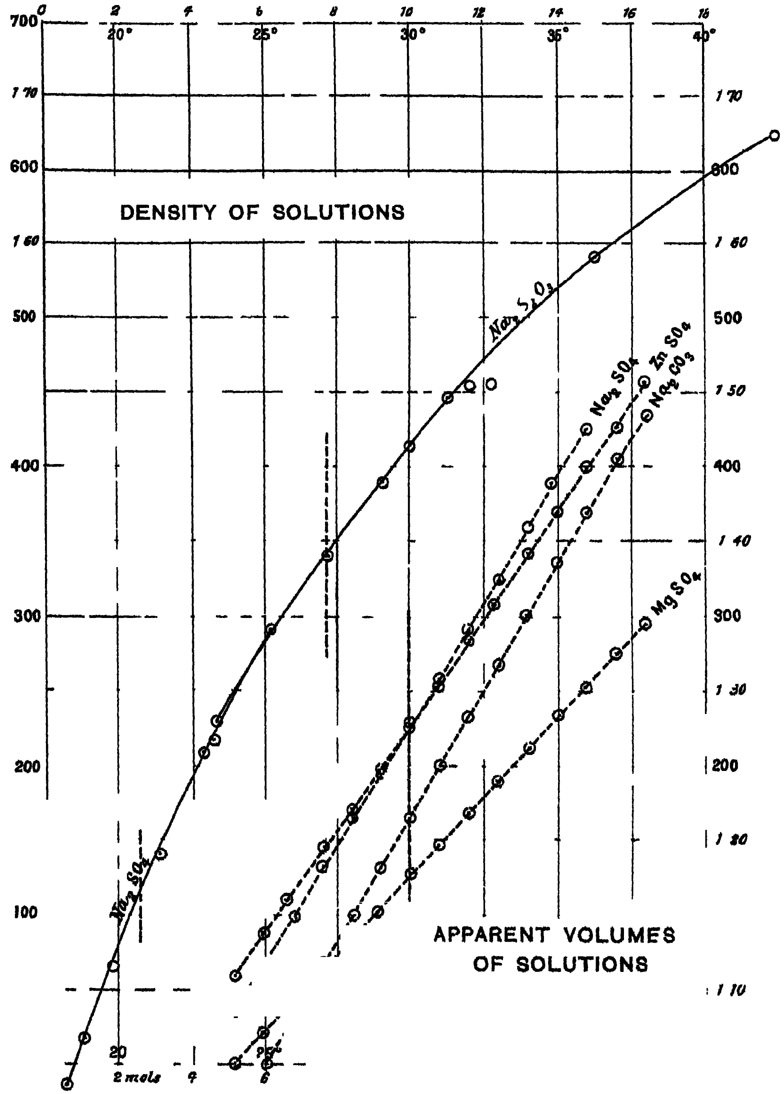
The thermal argument I have already treated of at some length in a previous paper (*Chem. News*, 1886, **54**, 1403), and I am still convinced that all the thermochemical results relating to Thomsen's "*Acidität*," or Ostwald's "*Affinität*," tend to prove by their concordance the non-existence of hydrates in solution.

The colour-changes are at first sight an insuperable difficulty, but I believe that as our knowledge of the phenomena of solution increases, we shall find that these are due, not to hydration or dehydration, but to some rearrangement of the molecule of the salt itself, similar it may be to the rearrangement in the case of chromium sulphate, but differing from it in being more easily reversed, in fact the experiments of Wagner (*Wied. Ann.*, 1883, **18**, 286) on the specific viscosity of copper chloride before and after heating lend much support to this view.

SPECIFIC VISCOSITY
T° VARYING
CONCENTRATION CONSTANT



Journ Chem Soc May 1887

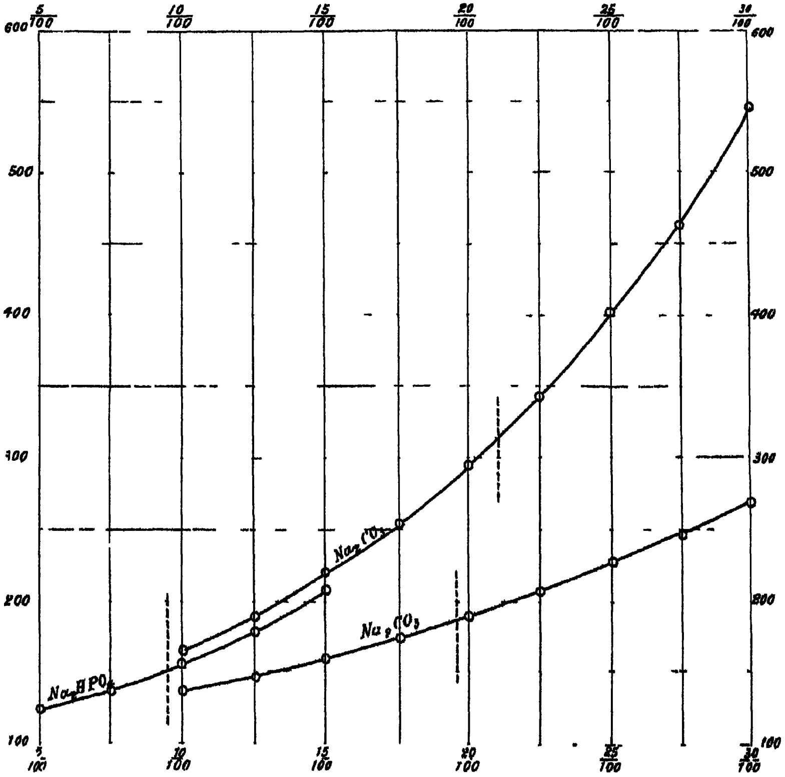


Lith M r Lan W C

Journ Chem Soc May 1887 NICOL

SPECIFIC VISCOSITY T° = 20°

CONCENTRATION VARYING



Harrison & Sons Lith St Martins Lane WC

XL.—*Action of Heat on Peroxide of Nitrogen.*

By Arthur Richardson, Ph.D., Assistant Lecturer, University College, Bristol.

Hitherto the decomposition of peroxide of nitrogen by heat has been studied only for temperatures below 180°. The change which this substance undergoes when heated from 4·2—97·5° was observed by Playfair and Wanklyn (*J. Chem. Soc.*, 1862, **15**, 156), who found that the density of the gas for the higher temperature is not far removed from that calculated from the formula NO_2, whilst that found for the lower temperature corresponds more nearly with the formula of the compound N_2O_4. Deville and Troost (*Compt. rend.*, **64**, 237) have also shown that at a temperature of 140°, N_2O_4 is completely dissociated into NO_2, whilst Nauman (*Ber.*, 1878, 2045) observed that at constant temperatures the amount of dissociation increases with diminished pressure, and for equal pressures increases with rise in temperature. Again F. and L. Natanson (*Ann. Phys. Chem.*, 1886, 606) have found that at −12°, and at a pressure of 115·4 mm. the vapour-density of the gas is 42·54, that calculated for N_2O_4 being 46.

It has been observed by Ramsay (Trans., 1885, 678) that nitric peroxide becomes colourless at a temperature below a red heat. The author finds that when the peroxide is heated in a glass tube over a Bunsen flame, the gas becomes almost colourless at a temperature a little above 500°; on allowing the tube to cool, the gas passes through a series of colour-changes similar to those observed on heating the tube, and finally assumes its original tint at the temperature of the air. A similar experiment was made with the gas under very great pressure; it was found that the amount of dissociation was diminished by increased pressure, for in this case no diminution in the intensity of the dark-red colour of the gas was perceptible at 500°.

When one limb of a bent glass tube containing the gas was strongly heated, whilst the other limb was immersed in a freezing mixture, a dark-blue liquid condensed in the cooled limb, while the liquid which condensed before the tube was heated was of a pale-yellow colour. On warming the tube gently, the blue colour of the liquid was changed to green, and finally became red; the blue colour could be again restored by cooling the tube in a freezing mixture, even after the rest of the tube had become cold. As this blue liquid is known to be nitrogen trioxide, produced by the union of nitric oxide with nitric peroxide, its formation appears to be a conclusive proof of the presence of nitric oxide as one of the dissociation products of the peroxide; it would appear also that the combination of nitric oxide with nitric peroxide takes place more readily than that of oxygen with nitric oxide, or of oxygen with the trioxide, provided there is an excess of the peroxide.

When the tube was opened immediately after heating, free oxygen was found to be present on testing the gas in the usual way. An experiment was then made to ascertain whether any further decomposition of the gas took place, and for this purpose a hard glass tube containing the peroxide was heated to between 600—700°, and then sealed. When the tube was opened under strong sulphuric acid, complete absorption of the gas took place, showing that no further decomposition of the nitric oxide had occurred.

It would appear then—

1. That nitric peroxide dissociates when heated into nitric oxide and free oxygen.

2. That nitric oxide, in presence of a large excess of peroxide, unites with the latter to form the trioxide more readily than it does with oxygen to form the peroxide; and that, under these conditions, recombination of nitric oxide with oxygen is complete only after some time, even at ordinary temperatures.

A series of quantitative experiments were then made, in order to ascertain the amount of dissociation which the peroxide undergoes at different temperatures. The peroxide was prepared by acting on arsenic trioxide with nitric acid to which an excess of strong sulphuric acid has been added, as recommended by Groves. The materials were heated gently in a retort with a drawn-out neck which dipped into a flask cooled in a freezing mixture, the condensed gas, which consisted of peroxide of nitrogen together with a considerable quantity of nitric acid, was then distilled by means of a water-bath, and the peroxide which passed over was condensed in a two-necked bulb containing phosphoric anhydride cooled in a freezing mixture.

When vapour ceased to distil over, the receiver was sealed, and shaken to bring the liquid in contact with the phosphoric anhydride, and allowed to stand for 12 hours; in order to remove all traces of impurities, it was distilled three times from fresh phosphoric anhydride, the gas being led through a U-tube containing the same substance. The liquid so obtained was sealed up in a bulb, and at ordinary temperatures was of a clear red colour, changing to a pale-yellow tint on being cooled. All connections of cork or india-rubber were avoided, the different parts of the distilling apparatus being sealed together. The vapour-density of the peroxide was determined by "Dumas' method," and when temperatures not higher than 358° were required the bulb was heated in the vapours of the following substances, which were known to be pure:—

Chlorobenzene, b. p. at 760 mm.	132·1° C.
Aniline, b. p. at 760 mm.	184·5
Methyl salicylate, b. p. at 760 mm.	223·0
Bromonaphthalene „ „	280·5
Triphenylmethane „ „	358·0

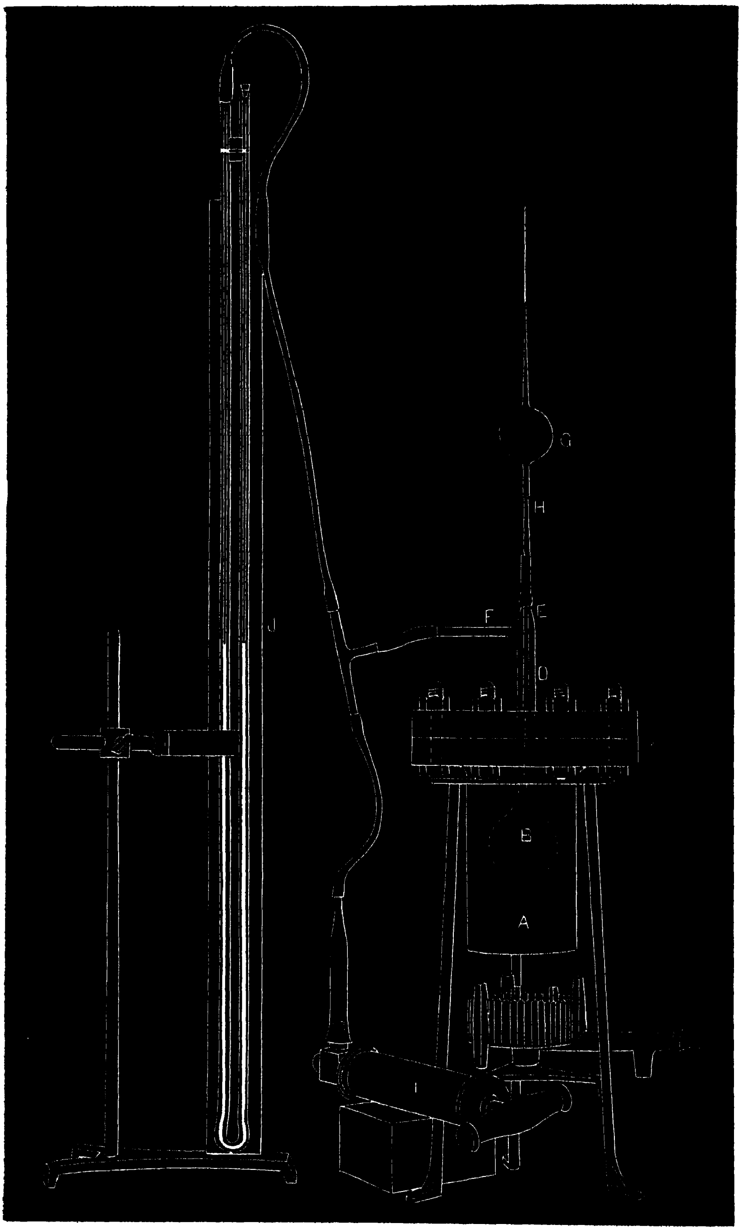
For higher temperatures, Ramsay and Young's method was adopted, that is to say, the required temperature was obtained by causing the substance to boil under known pressures higher or lower than that of the atmosphere; in this case, sulphur was used, the boiling points of which, under pressure between 500 and 2000 mm., has been accurately determined by Regnault.

The apparatus in which the bulb was heated consisted of an iron pot, A (see Fig. 1), having a grooved flange on the open end. This vessel was of such a size that the experimental bulb, B, could be suspended in it without coming in contact with the sides; the lid, C, was provided with a projection, which fitted into the grooves on the flange to which it was screwed by means of clamps; a wide glass tube, D, passed through the centre of the lid; this tube was drawn out at E *into* a narrow neck which was fitted with a stout piece of indiarubber tubing, through which passed the stem, H, of the experimental bulb, the two joints being carefully wired; a side tube was sealed on to D at F, which was connected with the air-pump I, and pressure gauge J. As far as possible the lid and glass tube were made airtight by means of white lead, but in order to avoid errors through leakage, a large receiver was connected with the apparatus; by this means the alteration in pressure produced by leakage was reduced to a minimum. To use the apparatus, the bulb was suspended in its place in the pot, which was previously charged with fragments of sulphur, the lid was then screwed down, and a sufficient amount of the cooled peroxide was poured into the bulb; next the required pressure was obtained by means of the air-pump, and the apparatus was heated till the sulphur boiled. As soon as the vapour appeared in the glass tube, the stem of the bulb was sealed off in the blowpipe, and the apparatus allowed to cool, the lid was then unscrewed, and the bulb removed, cleaned, and weighed.

As it was often a considerable time before the sulphur vapour rose in the tube, the chance of diffusion of the peroxide from the neck of the bulb was avoided, by fitting a second bulb, G, over the stem, which was drawn out to a long capillary at one end, this bulb remained full of the peroxide during the experiment.

The highest temperature that could be conveniently obtained by

FIG. 1.



Vapour-densities of Nitric Peroxide at Temperatures between 619·5° and 130°.

	Temperature.	Barometer.	Weight of gas in grams.	Volume of gas in c.c.	Vapour-density.	Per cent. of NO_2 molecules decomposed.
Bulb heated in Air-bath	619°·50	mm. 760·00	0·02682	19·57	15·300	100·00
Sulphur boiling under 1500·00 mm. pressure	494·40	742·00	0·09320	58·65	17·780	58·71
1500·00 " "	494·40	743·00	0·09361	58·47	17·980	55·84
1422·80 " "	490·00	761·00	0·14015	86·92	18·040	55·00
1325·00 " "	485·40	763·50	0·13988	87·72	17·840	57·84
1000·00 " "	466·30	755·50	0·10119	61·63	18·370	50·40
760·00 " "	448·25	760·00	0·15700	91·55	19·200	40·63
744·15 " "	447·00	744·15	0·11526	89·95	18·980	43·28
500·00 " "	423·20	739·68	0·16304	92·99	19·630	34·48
272·30 " "	390·00	740·00	0·17025	97·34	19·570	35·05
Triphenylmethane boiling under 769·50 mm. pressure	358·00	769·50	0·14833	78·34	21·190	17·09
Bromonaphthalene boiling under 733·00 mm. pressure	278·40	733·00	0·22290	115·82	21·530	13·57
741·50 " "	279·20	741·50	0·22557	116·56	21·590	13·10
Methyl salicylate boiling under 755·00 mm. pressure	222·50	755·60	0·19580	97·78	22·400	5·26
747·50 " "	222·10	747·50	0·26411	130·97	22·520	4·17
Aniline boiling under 758·10 mm. pressure	184·10	757·10	0·21210	106·15	22·350	5·80
752·00 " "	184·00	752·00	0·28743	143·47	22·450	4·33
Chlorobenzene boiling under 718·50 " "	130·00	718·50	0·32320	155·48	23·260	—

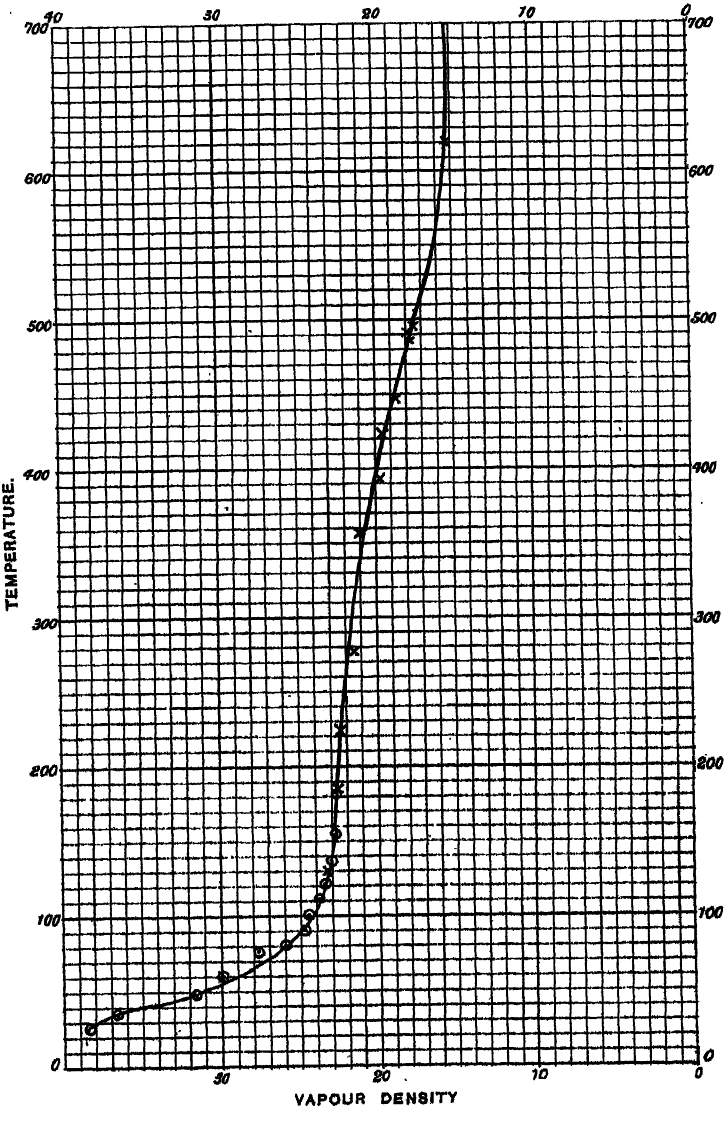
this method was 494·4°, that is, sulphur boiling under a pressure of 1500 mm. For higher temperatures, a cylindrical air-bath was used, and the temperature was indicated by means of an air-thermometer, which consisted of a hard glass tube drawn out into a narrow neck; the volume of this tube having been previously determined, it was suspended from the lid of the bath for 15 minutes, it was then sealed at the neck, and removed, and another tube at once substituted which contained a little of the liquid peroxide, this tube was allowed to take the temperature of the bath, and then sealed, and weighed when cold; finally the temperature was again taken by another air-tube similar to the first. The temperature was calculated by opening the air-tubes under water, from which all air had been expelled by prolonged boiling; the volume of residual air in the tubes was then found by weighing, the required data being obtained, the temperature could be calculated. Temperatures taken in this way agreed with each other within 10°, and by taking the mean of the temperatures given by several tubes, a pretty close approximation to the true temperature could be obtained. Tubes containing the peroxide, when removed from the bath heated to 620°, were perfectly colourless, the colour returning as the tubes cooled. The complete dissociation of the peroxide into nitric oxide and oxygen is represented by the equation $2NO_2 = 2NO + O_2$, the vapour-density of the peroxide being 23, that of the product 15·33.

From the experimental results given in the table (p. 401), it will be seen that at a temperature of 140° the vapour-density of the gas is expressed by the formula NO_2, whilst as the temperature rises, the number representing the vapour-density of the substance becomes smaller, and finally at a temperature of 619·5°, it corresponds with that of complete dissociation. It appears, then, that the peroxide undergoes dissociation in two distinct stages, giving a double dissociation curve, and that the dissociation of N_2O_4 into NO_2, which is complete at 140°, is immediately succeeded by a further dissociation of NO_2 into NO and O, which is complete below 620°. The form of the curve (Plates I and II) representing the second part of the change, is that usually exhibited by dissociating substances, the change of density being most rapid at the temperature at which half the total number of molecules of the original substance is decomposed.

In conclusion, I may add that on passing a series of electric sparks through the peroxide at the ordinary temperatures in a sealed glass tube, a white solid is deposited on the sides of the tube. This substance is also formed when the gas is heated to about 400°, also when a tube containing the liquid is exposed to sunlight for some months. No deposit was observed in tubes which had not been placed under one of these conditions.

CURVE SHOWING VAPOUR DENSITY OF NITRIC PEROXIDE

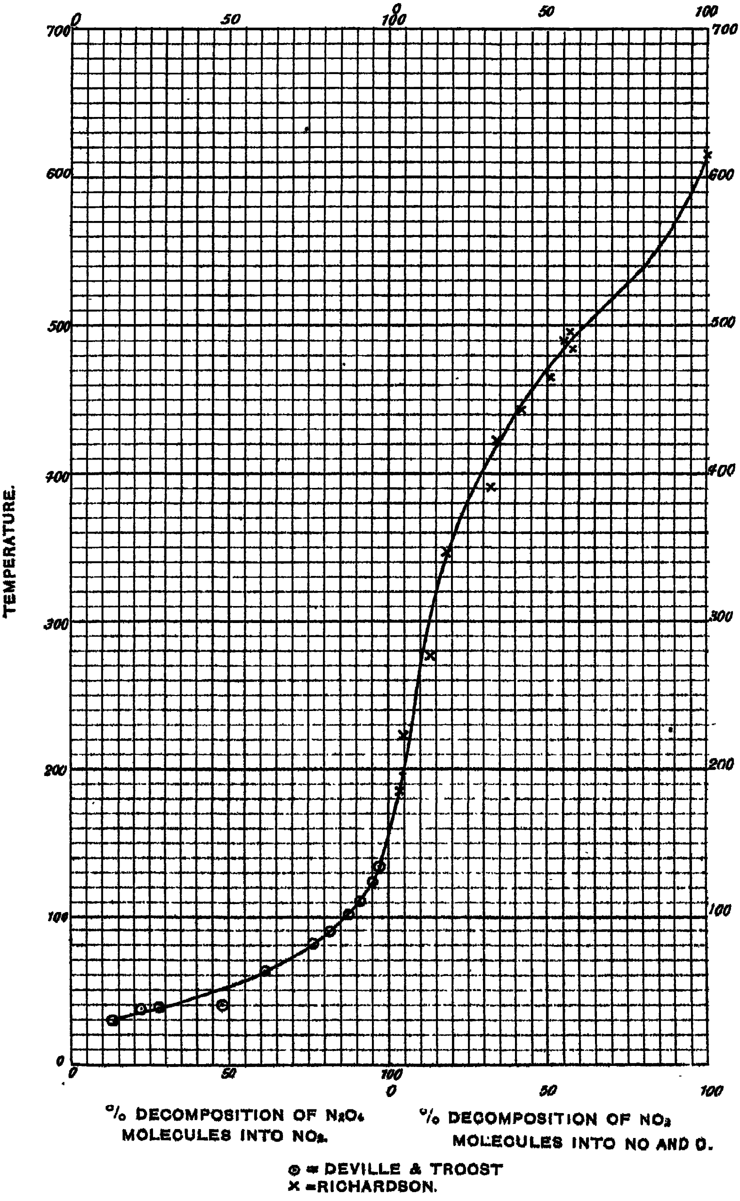
BETWEEN 25° AND 620°



⊙ = DEVILLE & TROOST
× = RICHARDSON

Journ. Chem. Soc. May 1887. RICHARDSON.

CURVE SHOWING % DECOMPOSITION OF N_2O_4 INTO NO_2, AND OF NO_2 INTO NO AND O.

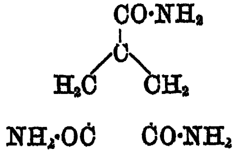


This substance was soluble in water, from which it could be again deposited on evaporation; at a temperature between 500° and 600°, it volatilised, but as it is only very sparingly formed enough of the substance has not yet been obtained for analysis.

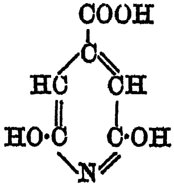
XLI.—*Formation of Pyridine-derivatives from Citric Acid, and on the Constitution of Pyridine.*

By Dr. S Ruhemann, Jacksonian Demonstrator in the University of Cambridge.

Two years ago Hofmann and Behrmann (*Ber.*, **17**, 2681) transformed the amides of citric acid into citrazinic acid, a derivative of pyridine, by the aid of sulphuric acid, the reaction which took place being represented by the following formulæ:—



Citramide.

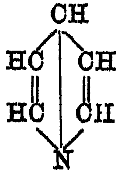


Citrazinic acid.

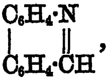
They further proved that the nitrogen-atom in this dihydroxypyridinecarboxylic acid is in the *para*-position to the carboxyl-group, by converting it into isonicotinic acid.

I desired to investigate more minutely the mode of formation of the pyridine nucleus, and to ascertain the influence of the hydroxyl-group of citramide in the reaction, especially with reference to its mode of removal. This inquiry is closely connected with the question of the constitution of pyridine.

During the last few years, objections to the old formula of pyridine have been raised by various chemists. When Riedel (*Ber.*, **16**, 1609) and then Bernthsen (*Ber*, **16**, 1971) brought forward their formula for acridine, the constitution of pyridine was surmised to be—



But Bernthsen and Bender admitted that the formation of acridine from diphenylamine and formic acid does not afford a convincing proof for this constitution of pyridine. And, further, Ladenburg (*Ber.*, **16**, 2063) has suggested that acridine may be represented by the following graphic formula:—



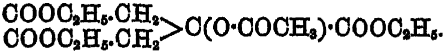
$$\begin{array}{l} C_6H_4{\cdot}N \\ |\qquad \| \\ C_6H_4{\cdot}CH \end{array},$$

from which the old formula of pyridine is deducible.

The theory that the nitrogen-atom of pyridine is directly linked to three carbon-atoms is supported by the important investigation of Hantzsch (*Ber.*, **17**, 1512) on the formation of pyridine-derivatives by the action of aldehyde ammonia on ethylacetoacetate. He established the fact that the aldehyde radicle enters into the pyridine nucleus in the *para*-position to the nitrogen-atom, and from this he concludes that pyridine is represented by the modified formula; this reaction can be explained, however, although with little probability, on the assumption that the aldehyde ammonia first decomposes, and then the components, aldehyde and ammonia, condense with the ethyl acetoacetate.

I hope, however, the following experiments will afford a conclusive proof of the correctness of the constitution suggested by Riedel.

My starting point was *ethyl citrate*. A good yield was obtained by using Conen's (*Ber.*, **12**, 1653) method of preparation, and I can corroborate this chemist's statement, that it is necessary to distil under diminished pressure. The citrate distils almost completely at 218°, under a pressure of 60 mm. When it is mixed with rather more than an equivalent quantity of acetic chloride, and warmed on a water-bath, it is converted into *ethyl acetylcitrate*,



$$\begin{array}{l} COOC_2H_5{\cdot}CH_2 \\ COOC_2H_5{\cdot}CH_2 \end{array}\!\!>C(O{\cdot}COCH_3){\cdot}COOC_2H_5.$$

The boiling point was found to be 288°, as given by Wislicenus (*Annalen*, **129**, 192), but at this temperature it turns brown, so that it is again advisable to distil under diminished pressure. It boils at 214°, press. 40 mm. (228—229° C., press. 100 mm.). Its sp. gr. at 15° is 1·1459, when referred to water at the same temperature.

On analysis the following numbers were obtained:—

	Theory.		Found.
C_{14}	168	52·83	53·00
H_{22}	22	6·92	6·91
O_8	128	40·25	
	318	100·00	

On slightly warming ethyl acetylcitrate with phenylhydrazine, crystals at once separate out. After recrystallisation from benzene, their melting point is 128°, which exactly coincides with that given by Fischer (*Annalen*, **190**, 129) for *acetylphenylhydrazine*. The analysis identified it.

The formula $C_6H_5 \cdot NH \cdot NH \cdot C_2H_3O$, requires the following numbers:—

	Theory.		Found.	
			I.	II.
C_8......	96	64·00	63·73	—
H_{10}	10	6·67	6·73	—
N_2	28	18·67	—	18 68
O......	16	10·66		
	150	100·00		

This result is of considerable importance, for it proved that the acetyl-group readily leaves the acetylcitrate. The following experiment points to the same conclusion.

Action of Ammonia on Ethyl Acetylcitrate.

On pouring strong aqueous ammonia on the ethyl acetylcitrate, it at once becomes yellow, and after standing for a few days, the oil entirely disappears, and the solution reddens. This red solution on exposure to the atmosphere develops a deeper tint, and begins to fluoresce, transmitting the green rays, and reflecting the red. If the acetylcitrate is perfectly pure, no crystals separate out, even after standing for several weeks. On one or two occasions a minute quantity of small yellow crystals was deposited; these could be recrystallised from hot water, but the amount of the substance at my disposal was too small for an investigation of their constitution. Most probably it is citramide derived from traces of ethyl citrate contained in the ethyl acetylcitrate.

On warming the red solution thus obtained on a water-bath, ammonia was given off, the colour of the solution deepened, and crystals separated; these, on being collected and washed with water, have the appearance of a grey powder. More crystals were obtained by concentrating the mother-liquor, which is deeply coloured; on further evaporation, a black resin remained, from which nothing crystalline could be extracted. The grey substance is easily soluble in ammonia, and therefore has acid properties; it is also somewhat basic, for it dissolves in strong hydrochloric acid, and is precipitated unchanged from the solution on diluting it with water. Its behaviour with these solvents affords a means of purifying it, for it can be dissolved in ammonia and precipitated with dilute hydrochloric acid; the analysis of the product, however, showed that the purification was incomplete (see III in the analytical results given below).

It can be obtained perfectly pure, however, by crystallising it from a large quantity of boiling water, when it separates in grey microscopical crystals, the solution turning dark brown on exposure to the air. The analysis, as well as its properties, prove that the substance is the amide of the citrazinic acid which Hofmann and Behrmann produced from citramide by means of sulphuric acid. I therefore call it *citrazinamide*.

The following equation represents its formation:—

$$C_{14}H_{22}O_8 + 3NH_3 = 3C_2H_5 \cdot OH + CH_3 \cdot CONH_2 + H_2O + C_6H_6N_2O_3.$$

The formula $C_6H_6N_2O_3$ requires the following numbers:—

	Theory.		Found.			
			I.	II.	III.	IV.
C_6......	72	46·75	46·6	46·34	46·08	—
H_6......	6	3·90	4·1	4·06	4·17	—
N_2......	28	18·18	—	—	—	18·19
O_3......	48	31·17	—	—	—	—
	154	100·00				

Citrazinamide possesses strongly acid properties, as was mentioned above. Its solubility in ammonia is characteristic of its behaviour with the other alkalis. Silver nitrate added to the ammoniacal solution produces a yellowish-white precipitate, which rapidly decomposes and darkens. Barium chloride or calcium chloride added to the ammoniacal solution throws down a slightly coloured crystalline precipitate.

The barium salt becomes yellow on drying in a vacuum over sulphuric acid, or at 100°. In both cases the analysis showed that it contains 2 mols. H_2O.

The formula $(C_6H_5N_2O_3)_2Ba + 2H_2O$ requires the following numbers:—

	Theory.	Found.		
		I.	II.	III.
Ba......	28·6 per cent.	28·8	28·85	—
N	11·7 ,,	—	—	11·75

Citrazinamide, like citrazinic acid, is a very stable compound; it is dissolved by strong sulphuric acid in the cold, and even after standing for several days it can be precipitated unchanged, as it is from its solution in hydrochloric acid.

The following nitrogen determination proves that it is not altered by this treatment:—

	Theory.	Found.
N........	18·18	18·19

It is not altered by digestion with methyl iodide and methyl alcohol for 4—5 hours at 100°, for on analysis it gave 18 per cent. N.

On distilling citrazinamide with zinc-dust, an oil with the distinct odour of pyridine was obtained. Lack of material prevented me from analysing this product. That citrazinamide is a derivative of pyridine, however, is sufficiently proved by its behaviour with hydrochloric acid. When this amide is heated in a sealed tube at 200—220° with strong hydrochloric acid, it is completely decomposed into a humus-like mass, with the formation of ammonium chloride; but if the amide is heated in an open vessel with concentrated hydrochloric acid, yellowish-brown crystals separate, and the liquid contains ammonium chloride. These crystals are *citrazinic acid.* Although this acid is only very sparingly soluble in water, it can be crystallised from a large quantity of boiling water. The colour of the crystals remains the same after several recrystallisations. Its properties as well as its analysis prove it to be citrazinic acid.

The formula $C_6H_5NO_4$ requires the following numbers:—

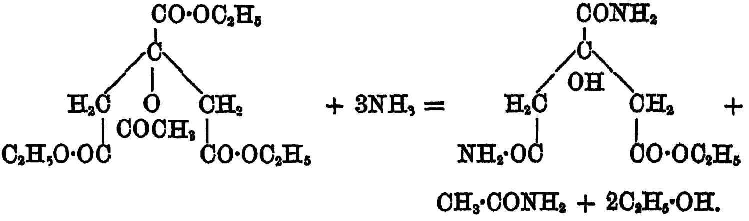
	Theory.		Found.	
			I.	II.
C_6........	72	46·45	46·00	—
H_5........	5	3·23	3·55	—
N........	14	9·03	—	9·26
O_4........	64	41·29	—	—
	155	100·00		

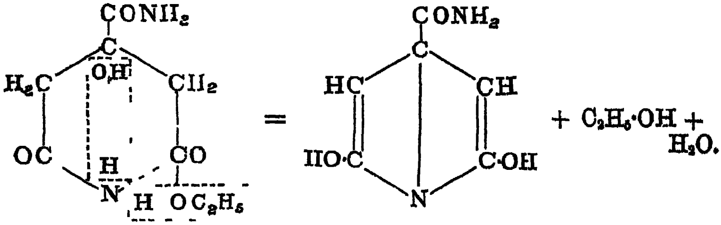
Hofmann and Behrmann found that citrazinic acid gave a blue coloration with a warm solution of potassium nitrite. These crystals also gave this coloration, as indeed did the aqueous mother-liquor.

This conversion of ethyl acetylcitrate into a derivative of pyridine seemed of sufficient importance to merit a fuller investigation. Does the action ensue on allowing the ethyl acetylcitrate to stand with aqueous ammonia in the cold, or are not the necessary conditions fulfilled until the ammoniacal solution is evaporated on the water-bath? These questions are easily answered. Citrazinamide could readily be obtained from the cold ammoniacal solutions without any warming, for on adding dilute hydrochloric acid a substance was thrown down which on analysis gave the numbers in II (see above, p. 406).

I believe this is the first time that citric acid has been directly converted into a derivative of pyridine under conditions analogous to those of plant life, for the pressure is atmospheric, and the temperature is merely that of the air, and above all no condensing agent, such as sulphuric acid, is used.

The details of this action can be traced by aid of the following graphical formulæ, which need no further explanation:—

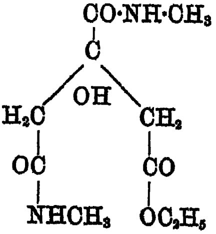




Whatever view may be taken of the process of the formation of citrazinamide from ethyl acetylcitrate by the action of ammonia, it follows that under the above conditions the nitrogen-atom must be directly linked to that carbon-atom which is in the para-position.

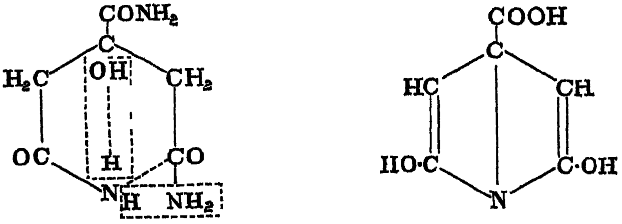
A further experiment was made with direct reference to this conclusion. The above experiments with ethyl acetylcitrate were repeated, using methylamine instead of ammonia. If the above explanation be correct, no analogous condensation would be possible, for with the nitrogen-atom there is no available hydrogen-atom connected, which, on removal with the hydroxyl-group, would allow the nitrogen-atom to link itself to the γ-carbon-atom.

An inspection of the graphic formula renders this deduction evident:—

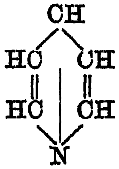


As a fact no condensation ensued. The product was a viscous oily mass.

The reaction which Hofmann and Behrmann (*loc. cit.*) discovered for the formation of citrazinic acid, may be explained as follows :—



If the above constitution for citrazinamide be accepted, the constitution of pyridine, by strict analogy, must be—



The above investigation, by showing that the introduction of the acetyl-group loosens the hydroxyl-group of ethyl citrate sufficiently to enable it to condense with ammonia, has opened a further field for research.

I am at present investigating the action of ammonia on ethyl acetylcitrate, and on ethyl diacetyltartrate, and hope to communicate the results of this work to the Society in a short time. I may mention that in these compounds the acetyl-group has the same freedom as in the ethyl acetylcitrate. This has been proved by the analogous formation of acetylphenylhydrazine in both cases.

XLII.—*On Silver containing Bismuth.*

By WILLIAM GOWLAND, Associate of the Royal School of Mines, Chemist and Assayer of the Imperial Mint, Osaka, Japan, and YOSHIMASA KOGA Assistant Assayer.

THE experiments recorded in this paper were made with the object of determining the effects produced by the presence of small quantities of bismuth on the ductility of silver, and on the uniformity of composition of silver bullion.

The silver bullion received in the Imperial Mint from certain Japanese mines and refineries, is occasionally found to be possessed of extraordinary brittleness. On melting this silver with its surface uncovered, and removing the slag formed from time to time, the brittleness disappears, a more or less prolonged exposure of the molten metal to the oxidising action of the air being required, according to the extent of the brittleness. On examining the slags formed during the early stages of the melting, they are found to consist chiefly of litharge, bismuthous oxide being present in but small amounts. As the oxidation proceeds the bismuthous oxide increases in quantity, until at the end of the process, when the silver has become tough, the slags are richly bismuthiferous. Every lot of brittle silver of high fineness which has been received during many years has been so melted and toughened, in some cases potassium nitrate being used to hasten the operation. The slags have been for some time frequently examined, and have always been found to contain bismuth but no other metals in proportions likely to cause brittleness. Arsenic and antimony have been repeatedly sought for, but have never been found in appreciable quantities.

An ingot weighing 651·24 troy oz. (20·2558 kilos.), which was brittle to an extraordinary degree—so much so that it broke into halves whilst a small cutting was being taken for assay from one edge of its base—was analysed, and found to be of the following composition:—

Silver	98·100
Gold	0·015
Bismuth	0·756
Lead	0·857
Copper	0·058
Iron	0·022
	99·808

The amount of lead present in this example might perhaps have been partially the cause of the brittleness, hence in order to demonstrate that bismuth alone is capable of inducing this property in silver, the following synthetical experiments were made.

Pure silver was melted with bismuth in the following proportions:—

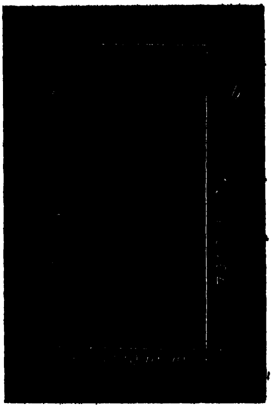
	I.	II.
Silver....	6·41 grams = 99 p. c.	6·45 grams = 99·5 p. c.
Bismuth.	0·06 „ = 1 „	0·03 „ = 0·5 „

The melting was carefully performed under charcoal in small clay crucibles,.and well melted buttons were obtained. The buttons in both cases were brittle, and were broken easily in a vice, without being first cut or nicked with a chisel. Their fractures were similar, dull, and minutely crystalline. When hammered or rolled, both alloys behaved in the same way. On hammering a piece, it cracked much at the edges, but on rolling, although at first the edges cracked, yet on cutting off the cracked portions and rolling further, the metal became slightly ductile.

On obtaining these results, another alloy was prepared. 194·4 grams of pure silver were melted with 2·98 grams of bismuth, giving a millesimal composition of silver, 984·89, bismuth 15·11, the silver being first melted under charcoal, and the bismuth added to the molten silver. After careful stirring the metal was poured into a small iron bar mould, yielding a bar measuring 82 mm. long, 44·5 mm. broad, and 6·3 mm. thick.

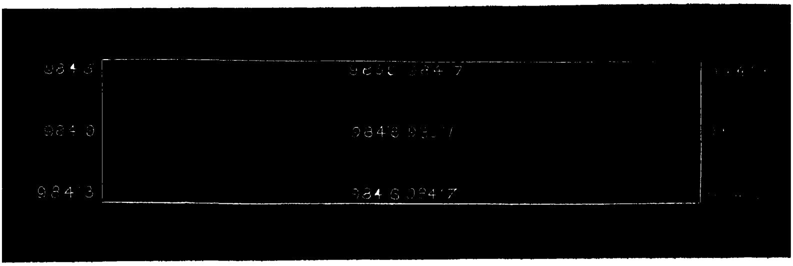
The bar was nicked slightly on the line AB (Fig. *a*), and broken in a vice. It broke easily, with a short, dull, minutely crystalline fracture.

FIG. *a*.



The longer portion was then rolled to a thickness of 2·5 mm., when it cracked too much for further rolling, the chief cracks extending very nearly to the middle of the strip, and minute cracks covering its entire surface. Assays were made of cuttings from several points in the rolled strip, in order to ascertain whether the bismuth had concentrated in any part during solidification. The results of the assays are given in Fig. *5*. From these it will be seen that there is slight concentration of silver in the middle of the bar.

FIG. *5*.



But as in such a small bar solidification must have taken place with great rapidity, and as different results may follow with larger masses under conditions of slower cooling, it was deemed advisable to operate on a larger scale, and to determine the effect exercised by the presence of small quantities of bismuth on the uniformity of the composition of silver bullion when in ingots of the size and form ordinarily met with in commerce. Also at the same time to ascertain from which part of an ingot an assay cutting should be taken so as to most accurately represent its mass.

To this end 1030·01 troy oz. (32·0369 kilos.) of silver were melted with 15·50 troy oz. (0·4821 kilo.) of bismuth, under the conditions and in the manner described below.

The silver consisted of two ingots, which assayed respectively 999·1 and 999·2 millesimal fineness.

The bismuth was the pure refined metal of commerce. It was found to contain only traces of gold, copper, nickel, and lead, and 1·8 per mille of silver.

The plumbago crucibles, covers, and stirrers were new.

The weight and composition of the charge were as follow:—

Ingot of silver	418 83	troy oz.	(13·02707 kilos.),	999·1 fineness.
„ „	611·18	„	(19·00983 „),	999·2 „
Bismuth	15·50	„	(0·4821 „)	containing 1·1 per mille of silver.

INGOT OF SILVER CONTAINING BISMUTH.

WEIGHT 1037 4 TROY Oz =32.2668 KILOGRAMS

SCALE $\frac{1}{4}$

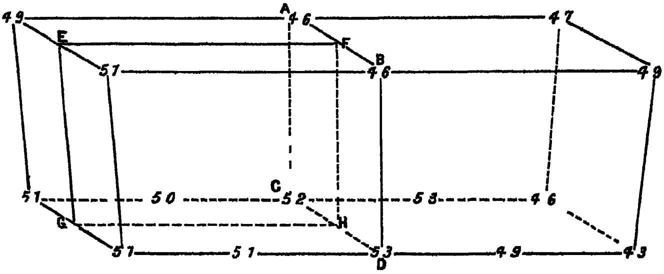


FIG 1

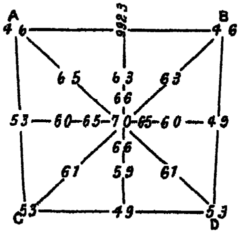


FIG 2 SECTION A B C D

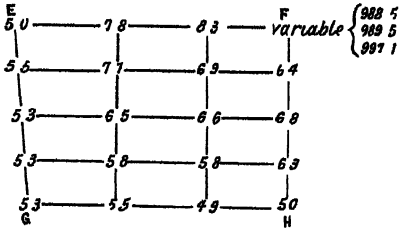


FIG 3 SECTION E F G. H

COMPOSITION OF GRANULATED DIP 985 5

The theoretical millesimal composition being—

Silver	984·37
Bismuth	14·80

The ingots of silver were melted under charcoal in a plumbago crucible, the bismuth, in small pieces, was added as soon as the silver was fluid, and thoroughly mixed with it by vigorous stirring with a plumbago stirrer. The crucible was then removed from the furnace, and its contents poured into an ordinary open iron ingot mould of rather more than 1000 oz. (31·103 kilos.) capacity. The ingot obtained measured 30·47 cm. long, 11·3 cm. broad at the top, 10·6 cm. at the bottom, and 10·1 cm. thick. Its upper surface was marked with transverse furrows, resembling in this respect the surface of ingots of refined copper. A narrow depression, about 17 mm. deep at its deepest part, extended along the middle portion of its median line. The ingot, after being cooled in water, was placed with its ends only resting on two iron blocks. On being then struck with a sledge-hammer, it broke after a few blows into two nearly equal pieces. The fractured surfaces showed a coarse crystallo-granular structure near their central parts, gradually becoming more and more largely crystalline towards the outer sides, where elongated columnar crystals extended inwards to a depth of 16 mm. from and at right angles to the cooling surfaces. There was a small cavity near the middle of the top of the ingot, just below the central depression, with crystals of the form of a four-sided pyramid with isosceles faces, the upper halves of distorted octahedra, projecting from its sides.

To ensure thorough admixture of the bismuth with the silver, the metal was again carefully melted and stirred, a new crucible and stirrer being used. A small quantity was dipped out and granulated in water for assay, and the metal was poured as before into the same mould.

The ingot weighed 1037·40 troy oz. (32·2667 kilos.). Portions of metal were taken from several parts, viz., one from each corner and three from each long edge of its base, and one from each corner and from each long edge of its top. On account of its great brittleness these could not be cut off in the usual way, as a single blow of the hammer caused the chisel to break off large and irregular lumps. Pieces of approximately equal size were obtained after some difficulty, and were assayed with the results shown in Fig. 1* in the plate. The numbers there given are the means of duplicate or triplicate assays made by a modification of the Gay-Lussac volumetric process.

---

* In this plate the figures 98 are usually omitted in stating the fineness; 5·3, for instance, meaning 985·3.

The granules taken as previously mentioned, and which hence represent the mass in composition, assayed 985·5 silver per mille. None of the parts assayed in Fig. 1 reach this fineness, yet from one or other of these it is customary to find assay pieces cut from ingots of bullion for their valuation. The mass is thus slightly richer in silver than an assay made from an ordinary cutting would indicate.

Hence, in silver—even of comparatively high fineness—suspected to contain bismuth, the portion required for assay should be taken from the metal whilst melted, and be granulated in water. Should it be impossible to melt the bullion, an assay piece cut from the middle of one of the long edges of the bottom of the ingot will give results approximating to its average composition. A bright brown resinous-like coating—bismuthiferous litharge—on cakes of silver from Japanese cupellation hearths, quite distinct in appearance from ordinary litharge, is an almost invariable indication of the presence of bismuth in injurious quantities.

A plate, A, B, C, D, Figs. 1 and 2, about 8 mm. in thickness, was then cut out transversely through the middle of the ingot by a slotting machine, and a similar plate, E, F, G, H, Figs. 1 and 3, longitudinally from the middle of one of the halves. Portions approximately in the form of cubes were taken from the points in these plates, shown in Figs. 2 and 3, and were assayed with the results there given.

All the pieces were brittle. Those from the sides and upper surfaces appeared to consist of an interlacing mass of loosely agglomerating columnar crystals which singly were ductile when hammered.

At the point F, Figs. 1 and 3 of the upper surface, just above a cavity containing crystals, the composition is extremely irregular. Disregarding this part, the difference between the two points of highest and lowest fineness, viz., 988·3 and 984·6, amounts to 3·7 per mille.

It will be seen from Figs. 1 and 2 that concentration of silver occurs generally throughout the internal portions of the upper two-thirds of the ingot, that is, in those parts which remained longest fluid, and notably along the median line of the upper surface. The ductility of the metal when rolled was tested in the following manner:—

A plate, measuring 90 mm. long, 33 mm. broad, and 8 mm. thick, was cut from one of the remaining parts of section E, F, G, H, Fig. 3; this was annealed at a dull red heat in an assay muffle, and then rolled. Soon after the commencement of the rolling, the edges became deeply jagged with cracks, but on continuing to roll these extended but little further inwards, and the metal was rolled down to a thickness of 0·5 mm. without destroying the continuity of the central portion.

This portion had in fact become ductile through the mechanical treatment, and could be bent almost completely over without fracture. It would thus appear that when the crystalline structure is once broken down ductility ensues. Hence the brittleness of silver containing bismuth is probably due to the crystalline structure which the presence of that metal induces in it.

Experiments were also made to ascertain the effect of bismuth on the ductility of silver coinage bars of 900 standard. A portion of the metal from the preceding experiments, weighing 370·72 oz. (11·5307 kilos.) was melted with the necessary quantity of electrotype copper, and cast into four bars, each measuring 58 cm. long, 4·35 cm. broad, and 1·25 cm. thick.

A portion taken from the molten metal, and granulated in water, assayed 899·6 silver per mille. One of the bars was slightly nicked with a chisel on one of its surfaces transversely 13 cm. from its upper and similarly 9 cm. from its lower extremity. At both points the bar broke at once on being struck with a heavy hammer. The fractured surfaces of both parts were somewhat conchoidal, dull, and non-crystalline. A bar of the same size and fineness prepared with refined silver, was similarly treated for comparison; it was broken with great difficulty, and bent to an angle of 30° before fracture. Its fractured surfaces were hackly. They were notably different in colour from those of the alloy containing bismuth, being white with only a faint fawn-coloured tinge, whilst in the latter they were distinctly reddish-fawn-coloured.

An attempt was made to roll the middle portion of the bismuthiferous bar, 31 cm. long, but it split before it was reduced to 9·5 mm. Two of the other bars split similarly, and could not be rolled. The fourth bar was then previously annealed, and after this treatment it was successfully rolled to 4·5 mm., again annealed, and then rolled to a thickness of 2·26 mm. without showing the slightest trace of cracks even at the edges. Three additional bars were prepared, and annealed, and rolled as the last, two rolled well and one broke; but the metal in all cases was hard and unsuitable for mintage.

The bismuthiferous silver which reaches the mint has been traced to three localities, viz.: Ikuno, in the province of Tajima; Odomi, in Hida; and Ani, in Ugo; at all of which it is obtained from argentiferous copper. At the Ikuno mine, according to Professor Milne, native bismuth has been found occasionally. At the others, no species of bismuth mineral has yet been identified. The copper produced at these mines contains small quantities of silver, generally sufficient to be worth extracting by liquation with lead. Any bismuth which may be present in the copper subjected to the liquation process is removed from it, together with the silver, by the lead. When the argentiferous lead is subsequently treated on cupellation hearths for the separation of the silver, part of the bismuth remains in the silver obtained.

A similar occurrence of bismuth in silver is mentioned by Dr. Percy (*Metallurgy of Lead*, pp. 201 and 202).

Summary.

α. When silver is obtained from copper containing bismuth by the liquation process with subsequent cupellation of the argentiferous lead, it contains part of the bismuth which was present in the copper.

β. This silver is brittle even when containing only small amounts of bismuth.

γ. Ingots of such silver are not uniform in composition throughout their mass, the parts which have remained longest fluid being richer in silver than the others.

δ. When coinage bars of 900 millesimal fineness are prepared with it, they cannot be rolled without special treatment, and even then are hard and unsuitable for mintage.

The Imperial Mint, Osaka, Japan,
22nd January, 1887.

XLIII.—*Suboxide of Silver*, Ag_4O.

By G. H. Bailey, D.Sc., Ph.D., and G. J. Fowler, B.Sc., The Owens College.

In the year 1839 Wöhler published a paper (*Annalen*, **30**, **1**) in which he announced the existence of a suboxide of silver having the composition Ag_4O. More recently incidental results bearing in the same direction have been published by von Bibra (*Berichte*, **8**, 741) and by Newbury "On a so-called Subchloride of Silver" (*Amer. Chem. J.*, **8**); up to the present time, however, no additional experimental evidence of a definite nature has been adduced which bears directly on the subject of Wöhler's experiments. It seemed desirable, therefore, more especially as the subject is one of some interest from a theoretical point of view, to re-examine this question, and the more so as preliminary experiments seemed to throw some doubt on Wöhler's deductions from his investigation. He states that on passing a stream of hydrogen over argentic citrate at 100°, the salt turns brown and is transformed into a mixture of argentous citrate and free citric acid, and that half the oxygen equivalent of the silver oxide is given off as water. He then extracted the free acid by washing the product with water until the washings began to assume a port-wine colour; the dark-brown powder which remained he found to be argentous citrate, and it yielded on ignition 76 per cent. of metallic silver, corresponding with the formula written according to the old notation, $Ag_2O,C_4H_4O_4$. In short, the reaction which takes place is according to him—

$$2(AgO,C_4H_4O_4) + H_2 = Ag_2O,C_4H_4O_4 + C_4H_4O_4 + H_2O.$$

It is remarkable that Wöhler should have interrupted the reaction just at a point where the numbers obtained suggest so definitely the formation of a subcitrate, for we were soon convinced that the reduction process is not of the simple character indicated by this equation, and that the product obtained varied according to the extent to which the reduction was allowed to proceed. A quantity of citrate of silver prepared in the usual manner was dried at 100°, at which temperature it showed no loss of weight, and was subsequently left in a desiccator over phosphorous pentoxide. The silver was determined by heating the salt for some time at 200° before igniting it, as otherwise its decomposition is accompanied by a slight explosion. The results of the analysis were:—

	Found.	Calculated.
Silver..................	63·15	63·15
Carbon	14·10	14·02
Hydrogen	1·08	0·97
Oxygen (by difference)	21·67	21·86

2·9075 grams of this salt was exposed for four hours to a current of dry hydrogen in a tube surrounded by a steam-jacket. The powder rapidly became reddish-brown and water was given off.

This reddish-brown powder contained 66·73 per cent. of Ag and 12·60 per cent. of C., whilst the residue left on extraction with water contained 68·04 per cent. of Ag and 11·95 per cent. of C. The total loss of weight was 0·0175 gram, of which the water obtained accounted for 0·012 gram. It was evident, therefore, that some product of the reaction was passing over in addition to water.

It had in fact escaped Wöhler's notice that considerable quantities of carbon dioxide are formed, and though the amount of this gas given off in the earlier stages of the reduction is small, yet at the point in the reduction at which his experiment was stopped this is by no means the case. Further experiments in which the silver salt was taken out from time to time and weighed, as well as the calcium chloride tube and potash bulbs attached to the apparatus, showed that the product obtained has a composition, dependent on the time during which the reduction continues. The amount of carbon dioxide and water formed at the later stages of course shows a diminution, but even after 36 hours the calcium chloride tube and potash bulbs still increased in weight. For instance, at the end of two hours, the powder from which the free acid had been extracted by water contained 66·08 per cent. of Ag, whilst at the end of 36 hours it had become much darker and yielded 85·80 per cent. of Ag, and contained much free silver. The amount of carbon dioxide had increased from a trace, to 3 per cent., and the water in a similar relation. Moreover, the amount of the aqueous extract showed a considerable increase, and at the end of the longer time amounted to nearly 20 per cent. of the original substance taken. This acid extract was subjected to examination, and it was found that, unlike citric acid, it was readily soluble in ether, and did not agree with citric acid in its behaviour with the ordinary reagents. In fact in the later experiments, instead of extracting with water, the dark brown powder was digested in a reversed condenser with anhydrous ether.

The yellow solution thus obtained was converted into the silver salt, and this, unlike citrate of silver, blackened very readily in the light, and was more freely soluble in hot water. It agreed in its characters with itaconic acid, though it was probably a mixture of several acids; the material at our disposal, however, did not admit of a further separation. The fact that carbon dioxide is evolved shows that either some citric acid is entirely decomposed, or, what is much more probable, independent of the support given by the qualitative reactions, a reduction product of citric acid is obtained.

From the results of our experiments, it would appear that, in the very early stages, water alone is given off with the production of aconitic acid, and that the reaction then proceeds further and brings about a reduction of this acid; there can be but little doubt that by exposing the citrate to hydrogen sufficiently long the insoluble residue would consist of metallic silver alone, thus :—

$$C_6H_5Ag_3O_7 = C_6H_3Ag_3O_6 + H_2O.$$

$$2C_6H_5Ag_3O_7 + 3H_2 = 2C_5H_6O_4 + 6Ag + 2CO_2 + 2H_2O.$$

We now pass to the consideration of the solution of the subcitrate prepared by Wöhler by treating the residue previously partially extracted with water for some time. This solution is, as he observed, of a port-wine colour, and through it passes with only slight alteration through a filter, this colour seems to be due to very finely divided suspended matter. Under a powerful beam of reflected light it appears dull and of a greenish tinge. On standing, the colour by transmitted light changes to greenish, then becomes brown, and finally almost black, when it begins to deposit a fine black powder. It contains, as a matter of fact, very little silver, and although Wohler prepares his suboxide by the addition of potash to this, he gives no determinations in support of the composition which he assigns to that compound, and such facts of a qualitative nature as are stated by him point more to its being a mixture of metallic silver with silver oxide. Metallic silver is unattacked by hydrochloric or citric acids, whilst oxide of silver dissolves with tolerable ease in excess of these acids; the precipitate obtained by potash was only partially attacked by either of these reagents, and the residue dissolved freely in nitric acid, giving off red fumes, and showed a metallic appearance under pressure.

Faraday's Suboxide.—Faraday (*Ann. Chim. Phys.*, 9, 107) observed that when silver oxide was dissolved in ammonia and exposed to the air, there separated a suboxide of silver to which he ascribed the composition Ag_4O_3; Wöhler left it undecided whether this oxide was identical with that obtained by him or not. We have prepared this compound by dissolving freshly precipitated oxide of silver in strong solution of ammonia in the cold, and allowing the solution to stand in a vacuum. It separates out in suboctahedral masses of an iron-grey colour, which float in the liquid and can be skimmed off the surface from time to time. It was always accompanied by a small quantity of fulminating silver, from which it could not be separated, and after being exposed some days considerable quantities of a yellow crystalline substance were also formed, the nature of which we have not further investigated. The presence of oxygen in the product was proved by heating some of it in a tube (in which the air had been displaced by carbon dioxide), and passing the gas given off into nitric oxide. The percentage of silver—

In Faraday's suboxide, Ag_4O_3	90·00
„ Wöhler's „ Ag_4O	96·42
„ ordinary oxide, Ag_2O	93·10
„ the product obtained above..........	92·34

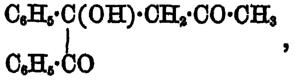
The substance is, therefore, a modified form of oxide of silver, the difference in the analysis being no doubt due to the small amount of fulminating silver present.

We have thus in the course of our experiments been unable to obtain any evidence of the formation of an argentous citrate in the manner described by Wöhler, or of the formation of a suboxide of silver.

XLIV.—*Anhydracetonebenzil.*

By FRANCIS R. JAPP, F.R.S., and COSMO INNES BURTON, B.Sc.

THE compound, *anhydracetonebenzil*, $C_{17}H_{14}O_2$, was prepared by Japp and Miller (Trans., 1885, 27) by the condensation of benzil with acetone under the influence of caustic potash. An additive compound, *acetonebenzil*,

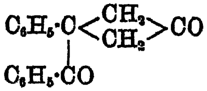


$$\begin{array}{l} C_6H_5\cdot C(OH)\cdot CH_2\cdot CO\cdot CH_3 \\ \quad\; | \\ C_6H_5\cdot CO \end{array},$$

is first formed, which, by the action of an excess of potash, parts with a molecule of water, yielding anhydracetonebenzil.* The fact that anhydracetonebenzil yields no acetic acid on oxidation (acetonebenzil readily yields acetic acid) was explained by supposing that the second methyl-group of the acetone had been modified during the condensation. It was also found that anhydracetonebenzil behaved towards bromine like a saturated compound, and further, that by limited oxidation it yielded an acid, $C_{16}H_{14}O_3$, according to the equation—

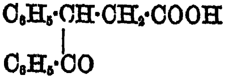
$$C_{17}H_{14}O_2 + 3O = C_{16}H_{14}O_3 + CO_2.$$

These reactions were believed to be best accounted for by the formulæ—

I. 

$$\begin{array}{l} C_6H_5\cdot C{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CO \\ \quad\; | \\ C_6H_5\cdot CO \end{array}$$

Anhydracetonebenzil.



$$\begin{array}{l} C_6H_5\cdot CH\cdot CH_2\cdot COOH \\ \quad\; | \\ C_6H_5\cdot CO \end{array}$$

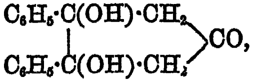
Acid.

But at the same time it was pointed out as not supporting this view, that this acid neither reacted with hydroxylamine, nor yielded a lactone on reduction, reactions which might be expected to occur, supposing it to have the above constitution.

There is, however, another way in which the formation of a saturated closed chain condensation-compound from acetonebenzil might be supposed to occur. Under the influence of the excess of potash the second methyl-group of the acetone in acetonebenzil might unite with the second carbonyl-group in the benzil portion of the molecule, and thus repeat the mode of combination by which acetonebenzil itself was formed. The resulting intermediate compound—

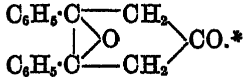
---

* In the first communication, this compound was named *dehydracetonebenzil.* The prefix "dehydro" is, however, ambiguous, being employed by some writers to denote *dehydration*, and by others to denote *dehydrogenation*, whereas "anhydro" is used in the former sense only.



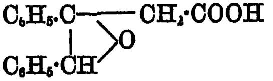
$$\left.\begin{array}{l} C_6H_5\cdot C(OH)\cdot CH_2 \\ \quad | \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{array}\right\rangle CO,$$

might then part with a molecule of water, yielding

II. 

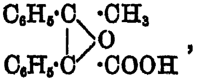
$$\left.\begin{array}{l} C_6H_5\cdot C\text{——}CH_2 \\ \quad |\rangle O \\ C_6H_5\cdot C\text{——}CH_2 \end{array}\right\rangle CO.^*$$

If this last formula were assigned to anhydracetonebenzil, the acid obtained from it by oxidation would have one of the two formulæ—



$$\begin{array}{l} C_6H_5\cdot C\text{——}CH_2\cdot COOH \\ \quad |\rangle O \\ C_6H_5\cdot CH \end{array}$$

, or



$$\begin{array}{l} C_6H_5\cdot C\;\cdot CH_3 \\ \quad |\rangle O \\ C_6H_5\cdot C\;\cdot COOH \end{array},$$

either of which would account for its inability to react with hydroxylamine.

Another argument, although not a very conclusive one, which might be advanced in favour of this second formula for anhydracetonebenzil is, that, unless both carbonyl-groups of benzil are concerned in the formation of the compound, there is no reason why benzaldehyde and acetone should not yield a compound analogous to anhydracetonebenzil (represented as in formula I), whereas they react to form an *unsaturated* compound, Claisen and Ponder's benzylideneacetone.

In view of the interest attaching at the present moment to the synthesis of closed carbon-chains, we have again taken up the study of anhydracetonebenzil, in order, if possible, to arrive at a clearer knowledge of its constitution. The compound is remarkable for the variety of definite transformations which it is capable of undergoing, but in spite of the number of new derivatives which we have prepared, we cannot claim to have finally solved the problem of its constitution. We have, however, obtained further evidence that it is a closed-chain compound, and have prepared the closed-chain hydrocarbon from which it is derived. Some of the reactions of anhydracetonebenzil are, moreover, of considerable interest in themselves, although we refrain for the present from discussing in detail the probable constitution of the compounds obtained.

---

* The molecule of water might be removed in other ways, but the resulting formula would not accord with the properties of anhydracetonebenzil as a saturated compound containing no hydroxyl-group.

Action of Phenylhydrazine.

When anhydracetonebenzil is heated with phenylhydrazine dissolved in methyl alcohol, it yields a compound which is sparingly soluble in boiling alcohol, and, on cooling, is deposited in tufts of slender yellow needles, melting with decomposition about 197°. A nitrogen estimation showed that the anhydracetonebenzil had reacted with only 1 mol. of phenylhydrazine:—

0·1110 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 21° and under 434 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 21° and under 399·2 mm. pressure.

	Calculated for $C_{17}H_{14}O(N_2H{\cdot}C_6H_5)$.	Found.
N in 100 parts	8·24	7·94

Anhydracetobenzil, heated with excess of phenylhydrazine in methyl alcohol solution at 150°, yielded the same compound, refusing to react with 2 mols. of phenylhydrazine.

Action of Reducing Agents.

Action of Hydriodic Acid at its Boiling Point.—Anhydracetonebenzil was boiled with an excess of fuming hydriodic acid for about five minutes. The substance partially fused, and caked together. The product was boiled with hydrogen sodium sulphite, to remove the iodine which had been liberated in the reaction, and was then dissolved in hot alcohol, in which it is very soluble. The cold solution very slowly deposited the new compound in long thin prisms of a yellowish-brown colour. This colour was only partially removed by boiling the solution with animal charcoal. It was found, however, that the substance could be dissolved in a very large volume of boiling water, whilst the brown resinous impurity remained undissolved. The filtered solution on cooling deposited the compound in very slender needles, which appeared colourless, but on recrystallising these needles from alcohol, the substance again separated in long thin prisms, with a very faint yellowish tinge, and melting constantly at 110°. Analysis gave figures agreeing with the formula $C_{17}H_{14}O$, showing that the compound had been formed from anhydracetonebenzil by the abstraction of an atom of oxygen:—

	Substance.	CO_2.	H_2O.
I	0·1172	0·3732	0·0633
II	0·1214	0·3870	0·0660

	Calculated for $C_{17}H_{14}O$.		Found.	
			I.	II.
C_{17}	204	87·18	86·86	86·90
H_{14}	14	5·98	6·00	6·04
O........	16	6·84	—	—
	234	100·00		

By heating the above compound with phenylhydrazine in alcoholic solution for some hours in a sealed tube at 100°, a substance was obtained which, on allowing the tube to cool, separated in yellow needles. After recrystallisation from boiling alcohol, in which it is only sparingly soluble, it formed rosettes of short yellow needles, melting with decomposition at 170—180°. A nitrogen determination gave figures agreeing with the formula $C_{17}H_{14}(N_2H{\cdot}C_6H_5)$:—

0·1107 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 20° and under 469·2 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 20·3° and under 430·2 mm. pressure.

	Calculated for $C_{17}H_{14}(N_2H{\cdot}C_6H_5)$.	Found.
N in 100 parts	8·64	8·62

The compound $C_{17}H_{14}O$ forms an additive compound with bromine, which, however, readily decomposes, and was not further examined.

Action of Hydriodic Acid and Amorphous Phosphorus.—Anhydracetonebenzil was heated in sealed tubes with fuming hydriodic acid and amorphous phosphorus for about six hours, at 130°. The tubes contained an oil, which was dissolved in ether, filtered from amorphous phosphorus, and, after expelling the ether, distilled in a vacuum. A pale-yellow oil was obtained, which in a freezing mixture solidified to a hard crystalline mass, the solid substance showing no tendency to melt at ordinary temperatures. It was dissolved in boiling alcohol, but on cooling separated as an oil. A quantity of alcohol nearly sufficient to keep the oil in solution in the cold, was therefore employed, and, as the solution cooled, a little of the solid substance was added. In this way the compound was obtained in colourless long flat needles, with a constant melting point of 47°. Under ordinary pressures it boils, with partial decomposition, at 305° (uncorr.).

The compound is a hydrocarbon. Analyses agreed with the formula $C_{17}H_{18}$:—

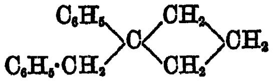
	Substance.	CO_2.	H_2O.
I	0·1553	0·5216	0·1138
II	0·1017	0·3420	0·0750

	Calculated for $C_{17}H_{18}$.		Found.	
			I.	II.
C_{17}	204	91·89	91·59	91·71
H_{18}	18	8·11	8·14	8·19
	222	100·00		

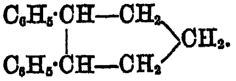
This hydrocarbon is formed from anhydracetonebenzil, according to the equation—

$$C_{17}H_{14}O_2 + 4H_2 = C_{17}H_{18} + 2H_2O.$$

This hydrocarbon would have either the first or the second of the following formulæ:—



Phenylbenzyl-tetramethylene (1, 1).



Diphenyl-pentamethylene (1, 2).

according as we assign to anhydracetonebenzil formula I or formula II (*ante*). We are at present unable to decide between these two views.

A third possibility is, that the hydrocarbon is a diphenylamylene, an open-chain compound. On this assumption it ought to be capable of combining with a further molecule of hydrogen to form a diphenylpentane, $C_{17}H_{20}$. We therefore heated anhydracetonebenzil with hydriodic acid and amorphous phosphorus at 150° for several hours, but obtained only the same hydrocarbon, $C_{17}H_{18}$. It is highly improbable that an unsaturated hydrocarbon would resist this treatment.

Towards bromine the substance also exhibited the behaviour of a saturated compound. When a solution of bromine in chloroform was added to a chloroform solution of the hydrocarbon, the colour of the bromine did not become perceptibly paler until after some time, and although all the materials had been carefully dried, this change was accompanied from the first by an evolution of hydrobromic acid. The quantity of hydrocarbon at our disposal did not suffice for a more thorough study of the action of bromine.

As already mentioned, the hydrocarbon undergoes partial decomposition when distiled under ordinary pressures. For this reason, determinations of the vapour-density by Victor Meyer's method in an atmosphere of nitrogen gave too low results.

Action of Tin and Hydrochloric Acid.—5 grams of anhydracetonebenzil were dissolved in alcohol and reduced with tin and hydrochloric acid. The action was allowed to go on for some days in the cold, after which the mixture was warmed for some time. The substance was precipitated with water, dried, and dissolved in benzene. On adding petroleum to the benzene solution, a crystalline substance gradually separated; this was recrystallised, first from benzene, and finally from alcohol, which deposited it in colourless lustrous minute rhomboidal plates, melting constantly at 187—188°. It is only sparingly soluble, even in hot alcohol. From benzene, in which it dissolves more readily, it separates in rosettes of short needles. The yield was very poor, and we were unable to increase it in subsequent experiments.

Analysis gave figures which led to the formula $C_{34}H_{34}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·1322	0·4171	0·0852
II	0·1159	0·3653	0·0741

	Calculated for $C_{34}H_{34}O_2$.		Found.	
			I.	II.
C_{34}	408	86·08	86·05	86·04
H_{34}	34	7·17	7·16	7·10
O_2	32	6 75	—	—
	474	100·00		

This compound is formed according to the equation—

$$2C_{17}H_{14}O_2 + 5H_2 = C_{34}H_{34}O_2 + 2H_2O,$$

and seeing that it is obtained by the action of nascent hydrogen on a ketone, with union of 2 mols. of the ketone, it is probably a pinacone. The poorness of the yield quite precluded a study of its reactions.

Action of Hot Dilute Sulphuric Acid.

Ten grams of anhydracetonebenzil were boiled for half an hour with a mixture of 50 c.c. of sulphuric acid with 100 c.c. of water. The substance gradually fused to an oil, which floated on the surface of the liquid and, on cooling, solidified. The solid cake was washed with water, and dissolved in hot benzene, which deposited it in lustrous thick prisms. The substance crystallises from benzene in two forms: one with, the other without, benzene of crystallisation. By repeated crystallisation it was obtained pure, and, when free from benzene, melted with decomposition at 195—200°, evolving gas. It is sparingly soluble in hot alcohol, and separates in short, flat, colourless prisms without alcohol of crystallisation.

The specimen analysed had been crystallised from benzene and dried at 120°. The analytical figures showed that a molecule of anhydracetonebenzil had parted with a molecule of water; but the behaviour of the compound on heating (*vide infra*) leads us to double the formula to $C_{34}H_{24}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·1111	0·3571	0·0523
II	0·1165	0·3752	0·0557

	Calculated for $C_{34}H_{24}O_2$.		Found.	
			I.	II.
C_{34}	408	87·93	87·66	87·82
H_{24}	24	5·17	5·22	5·31
O_2	32	6·90	—	—
	464	100·00		

The compound is formed according to the equation—

$$\underset{\text{Anhydracetonebenzil.}}{2C_{17}H_{14}O_2} = C_{34}H_{24}O_2 + 2H_2O.$$

This substance does not react with phenylhydrazine.

Action of Heat on the Compound, $C_{34}H_{24}O_2$.—In order to ascertain the nature of the decomposition which it underwent in melting, a quantity of this compound was introduced into a glass bulb, after which the bulb was attached to a Sprengel pump, exhausted, and then heated in a paraffin-bath at 200—205° as long as gas was evolved. The gas proved to be pure carbonic oxide. It burnt with the blue carbonic oxide flame, and was completely absorbed by a solution of cuprous chloride in hydrochloric acid. The substance in the bulb solidified on cooling to a pale-yellow vitreous mass, which readily dissolved in hot benzene, and was deposited in rectangular plates—generally with one corner slightly truncated—and containing benzene of crystallisation. It was recrystallised from the same solvent until it showed, after expelling the benzene, the constant melting point 162—163°. It is sparingly soluble in boiling alcohol; the solution on cooling deposits small, lustrous, well-developed crystals, apparently monosymmetric, not containing alcohol of crystallisation.

Analysis of the substance, crystallised from benzene and dried at 120°, gave figures pointing to the formula $C_{33}H_{24}O$:—

	Substance.	CO_2.	H_2O.
I	0·2137	0·7106.	0·1072
II	0·1839	0·6105	0·0936

	Calculated for $C_{33}H_{24}O$.		Found.	
			I.	II.
C_{33}	396	90·83	90·68	90·54
H_{24}	24	5·50	5·57	5·65
O........	16	3·67	—	—
	436	100·00		

Benzene of crystallisation was determined with the following result: Loss on heating air-dried substance at 100°, 15·63 per cent.; calculated for $C_{33}H_{24}O,C_6H_6$: C_6H_6 15·17 per cent.

The compound is formed according to the equation—

$$C_{34}H_{24}O_2 = C_{33}H_{24}O + CO,$$

and this reaction leads us to attribute to the compound from anhydracetonebenzil and sulphuric acid the formula $C_{34}H_{24}O_2$, instead of $C_{17}H_{12}O$, as it is highly improbable that 2 mols. of a compound, $C_{17}H_{12}O$, could, between them, yield the products formed in this reaction. The sparing solubility of the compound $C_{34}H_{24}O_2$ in alcohol, as compared with the ready solubility of anhydracetonebenzil, also speaks for the higher molecular weight.

In order to ascertain how far the foregoing equation was a quantitative expression of the decomposition, a weighed quantity of the compound $C_{34}H_{24}O_2$ was heated as above at 200° in an exhausted bulb attached to the Sprengel pump, the evolved gas pumped off and measured in a Frankland and Ward's gas-analysis apparatus, and the loss of weight of the substance determined. The following results were obtained:—

Weight of substance taken	1·0314 gram.
Loss of weight	0·0630 ,,

Volume of CO = 57·7 c.c. at 16·3° and under 689 mm. pressure, corresponding with 49·4 c.c. at 0° and 760 mm.

These numbers agree almost exactly with those calculated from the above equation:—

	Calculated.	Found.
Vol. of CO from 1·0314 gram substance.	49·6 c.c.	49·4 c.c.
Loss of weight......................	6·03 p. c.	6·11 p. c.

This is a remarkable reaction. We know of no other case in which an organic compound breaks up quantitatively into carbonic oxide and a perfectly definite, new organic compound—the latter being obtained forthwith in a nearly pure state. The relatively low temperature (200°) at which the decomposition occurs is also noteworthy.

	Calculated for $C_{33}H_{24}O$.		Found.	
			I.	II.
C_{33}	396	90·83	90·68	90·54
H_{24}	24	5·50	5·57	5·65
O........	16	3·67	—	—
	436	100·00		

Benzene of crystallisation was determined with the following result: Loss on heating air-dried substance at 100°, 15·63 per cent.; calculated for $C_{33}H_{24}O,C_6H_6$: C_6H_6 15·17 per cent.

The compound is formed according to the equation—

$$C_{34}H_{24}O_2 = C_{33}H_{24}O + CO,$$

and this reaction leads us to attribute to the compound from anhydracetonebenzil and sulphuric acid the formula $C_{34}H_{24}O_2$, instead of $C_{17}H_{12}O$, as it is highly improbable that 2 mols. of a compound, $C_{17}H_{12}O$, could, between them, yield the products formed in this reaction. The sparing solubility of the compound $C_{34}H_{24}O_2$ in alcohol, as compared with the ready solubility of anhydracetonebenzil, also speaks for the higher molecular weight.

In order to ascertain how far the foregoing equation was a quantitative expression of the decomposition, a weighed quantity of the compound $C_{34}H_{24}O_2$ was heated as above at 200° in an exhausted bulb attached to the Sprengel pump, the evolved gas pumped off and measured in a Frankland and Ward's gas-analysis apparatus, and the loss of weight of the substance determined. The following results were obtained:—

Weight of substance taken	1·0314 gram.
Loss of weight	0·0630 „

Volume of CO = 57·7 c.c. at 16·3° and under 689 mm. pressure, corresponding with 49·4 c.c. at 0° and 760 mm.

These numbers agree almost exactly with those calculated from the above equation:—

	Calculated.	Found.
Vol. of CO from 1·0314 gram substance.	49·6 c.c.	49·4 c.c.
Loss of weight.....................	6·03 p. c.	6·11 p. c.

This is a remarkable reaction. We know of no other case in which an organic compound breaks up quantitatively into carbonic oxide and a perfectly definite, new organic compound—the latter being obtained forthwith in a nearly pure state. The relatively low temperature (200°) at which the decomposition occurs is also noteworthy.

Simultaneous elimination of carbonic oxide and water from an organic compound is of course common enough.

When heated in a sealed tube at 100° with phenylhydrazine in methyl alcohol solution, the compound yields a derivative,

$$C_{34}H_{24}(N_2H{\cdot}C_6H_5),$$

which crystallises in pale-yellow slender needles, very sparingly soluble in alcohol, melting at 250°, if heated in a sealed capillary tube so as to prevent oxidation. A nitrogen determination gave the following result:—

0·1824 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 19·4° and under 482·2 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 19·4° and under 458·7 mm. pressure.

	Calculated for $C_{34}H_{24}(N_2H{\cdot}C_6H_5)$.	Found.
N in 100 parts	5·32	5·49

It is worthy of note that the parent compound, $C_{34}H_{24}O_2$, does not react with phenylhydrazine.

Action of Hydrochloric Acid.

Anhydracetonebenzil was dissolved in the cold in strong alcoholic hydrochloric acid (in which it is much more soluble than in pure alcohol), and allowed to stand for 24 hours, after which the dark-coloured liquid was poured into water. The precipitated substance was recrystallised several times from hot alcohol, and was thus obtained in colourless flat needles, with a silky lustre, melting at 128°. It was found to contain chlorine. Analysis gave figures agreeing with the formula $C_{17}H_{13}ClO$:—

	Substance.	CO_2.	H_2O.
I	0·2078	0·5773	0·0928
II	0·2389	0·6613	0·1056

III. 0·4040 gram gave 0·2170 gram AgCl (by lime method).

	Calculated for $C_{17}H_{13}ClO$.		Found.		
			I.	II.	III.
C_{17}	204	76·00	75·76	75·49	—
H_{13}	13	4·84	4·96	4·91	—
Cl........	35·5	13·21	—	—	13·28
O	16	5·95	—	—	—
	268·5	100·00			

The compound is formed from anhydracetonebenzil according to the equation—

$$C_{17}H_{14}O_2 + HCl = C_{17}H_{13}ClO + H_2O.$$

This reaction would suggest that a hydroxyl-group in anhydracetonebenzil had been displaced by chlorine; but it appears that anhydracetonebenzil does not contain hydroxyl: thus it does not react with acetic anhydride. The compound $C_{17}H_{13}ClO$ may, however, be derived from a labile modification of anhydracetonebenzil.

Action of Ammonia on the Compound $C_{17}H_{13}ClO$.—When the foregoing compound is heated with alcoholic ammonia in a sealed tube at 100° for about two hours it yields a product identical with that obtained by the action of dilute sulphuric acid on anhydracetonebenzil. Like the latter, it crystallises in lustrous flat prisms, melting with evolution of gas at 195—200°. It is formed according to the equation—

$$2C_{17}H_{13}ClO = C_{34}H_{24}O_2 + 2HCl.$$

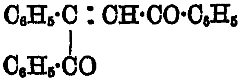
Oxidation with Nitric Acid.

This experiment was undertaken in the hope of obtaining a better yield of the oxidation product $C_{16}H_{14}O_3$ (Trans., 1885, 30), a study of which would doubtless throw light on the constitution of anhydracetonebenzil. This product was, however, not formed. When boiled for 10 minutes with dilute nitric acid (nitric acid of sp. gr. 1·42 with an equal volume of water), the anhydracetonebenzil underwent oxidation, yielding chiefly benzoic acid, together with paranitrobenzoic acid,* oxalic acid, benzil, and a small quantity of a neutral nitrogenous substance, soluble both in boiling water and in benzene, and crystallising in tufts of needles (m. p. 264°). The regeneration of benzil in this reaction is important, as showing that the benzil residue is present in anhydracetonebenzil, and that no migration, such as is involved in the formation of potassium benzilate from benzil and caustic potash, occurs in the formation of this compound. The otherwise conceivable possibility that anhydracetonebenzil is a diphenylmethane-derivative, formed from the benzil under the influence of the caustic potash, is thus excluded.

We have also, in connection with the above subject, undertaken the study of the reactions of *anhydracetophenonebenzil*, which was assumed by Japp and Miller (Trans., 1885, 37) to be an unsaturated open-chain compound of the formula

---

* A similar formation of *para*nitrobenzoic acid was observed by Claus (*Ber.*, 15, 2331) in the oxidation of amarine with dilute nitric acid.



$$\begin{array}{l} C_6H_5\cdot C : CH\cdot CO\cdot C_6H_5 \\ \quad\;\; | \\ C_6H_5\cdot CO \end{array}$$

A compound of this type ought to behave differently from anhydracetonebenzil. As a fact, it was shown (*loc. cit.*) that it forms an unstable additive compound with 4 atoms of bromine.

Anhydracetophenonebenzil appears to react both with 1 and with 2 mols. of phenylhydrazine, but neither of the derivatives thus formed could be obtained free from the other.

When boiled with fuming hydriodic acid for a few minutes, it is transformed like anhydracetonebenzil, parting with an atom of oxygen and yielding a compound, $C_{22}H_{16}O$. The product of the reaction was boiled with hydrogen sodium sulphite to remove iodine, and recrystallised from boiling alcohol, which deposited it in colourless, long, flat prisms melting constantly at 92—93°.

	Substance.	CO_2.	H_2O.
I	0·2004	0·6515	0·0992
II	0·1979	0·6433	0·0976

	Calculated for $C_{22}H_{16}O$.		Found.	
			I.	II.
C_{22}	264	89·19	88·66	88·65
H_{16}	16	5·40	5·50	5·48
O........	16	5·41	—	—
	296	100·00		

In its character of an unsaturated open-chain compound, anhydracetophenonebenzil should yield a triphenylbutane, $C_{22}H_{22}$, on heating with hydriodic acid and amorphous phosphorus in a sealed tube, and would thus differ in its behaviour from anhydracetonebenzil, which is not reduced to a phenyl-paraffin. This experiment was tried, but the resulting product of reduction is difficult to obtain in a crystallised state, and has not yet been further examined.

We did not succeed in splitting off water from anhydracetophenonebenzil by boiling it with dilute sulphuric acid.

With alcoholic hydrochloric acid, anhydracetophenonebenzil behaves like anhydracetonebenzil—

$$\underset{\text{Anhydracetophenonebenzil.}}{C_{22}H_{16}O_2} + HCl = C_{22}H_{15}ClO + H_2O.$$

The concentrated solution of hydric chloride in alcohol dissolves the substance slowly in the cold, at the same time becoming dark coloured, and on standing the liquid solidifies to a magma of crystals.

By recrystallisation from boiling alcohol, the new compound was obtained in colourless slender needles melting at 115°. A chlorine determination (Carius) gave the following result:—

0·2701 gram substance gave 0·1192 AgCl.

	Calculated for $C_{22}H_{15}ClO$.	Found.
Cl in 100 parts................	10·74	10·91

This investigation will be continued.

Normal School of Science,
South Kensington.

XLV.—*Condensation Compounds of Benzil with Ketones.*

By Francis R. Japp, F.R.S., and Cosmo Innes Burton, B.Sc.

In order to ascertain whether the reaction in which anhydracetonebenzil and anhydracetophenonebenzil are formed (see preceding paper) is of general application, we have examined the action of benzil with various homologues of acetone. Caustic potash of sp. gr. 1·27 was used as the dehydrating agent. In every case 1 mol. of benzil was found to react with 1 mol. of the ketone, eliminating 1 mol. of water. The intermediate additive compounds, the formation of which was observed in the reactions of benzil with acetone and acetophenone (Japp and Miller, Trans., 1885, 21 and 34), were not isolated.

For purposes of nomenclature we have *assumed* that the compounds about to be described are true homologues of anhydracetonebenzil. Thus the compound $C_{22}H_{24}O_2$, obtained from methyl hexyl ketone and benzil, will receive the name *amyl-anhydracetonebenzil.*

Methyl-anhydracetonebenzil, $C_{18}H_{16}O_2$.

70 grams of finely-powdered benzil, 25 grams of methyl ethyl ketone,* and 10 c.c. of caustic potash solution of the above strength, were allowed to stand in a corked flask at a temperature of 20—25° for some days, shaking the flask from time to time. In about a week the mixture solidified to a greyish-yellow mass, which was well washed with boiling water, treated with ether to remove unaltered benzil, and

---

* Prepared by Kahlbaum from ethylic methaceto-acetate by Böcking's method (*Annalen*, **204**, 17).

finally recrystallised from boiling alcohol. By repeated recrystallisation it was obtained in colourless thin prisms melting at 179°.

	Substance.	CO_2.	H_2O.
I	0·1830	0·5465	0·1025
II	0·1659	0·4958	0·0935

	Calculated for $C_{18}H_{16}O_2$.		Found.	
			I.	II.
C_{18}	216	81·82	81·44	81·50
H_{16}	16	6·06	6·22	6·26
O_2........	32	12·12	—	—
	264	100·00		

Dimethyl-anhydracetonebenzil, $C_{19}H_{18}O_2$.

Benzil	60 grams.
Diethyl ketone*....................	25 „
Caustic potash solution (sp. gr. 1·27)..	10 c.c.

Treatment and purification as in the case of methyl-anhydracetonebenzil. The new compound crystallised from alcohol in colourless, thick, rhomboidal plates, melting at 150°.

	Substance.	CO_2.	H_2O.
I	0·1538	0·4612	0·0902
II	0·1420	0·4264	0·0834

	Calculated for $C_{19}H_{18}O_2$.		Found.	
			I.	II.
C_{19}	228	82·01	81·78	81·90
H_{18}	18	6·48	6·52	6·53
O_2	32	11·51	—	—
	278	100·00		

Ethyl-anhydracetonebenzil, $C_{19}H_{18}O_2$.

Benzil............................	50 grams
Methyl propyl ketone†.............	25 „
Caustic potash solution (sp. gr. 1·27)..	10 c.c.

---

* Prepared by Kahlbaum from barium propionate by Krafft's method.

† From Kahlbaum. Obtained from crude wood-acetone. Further fractioned by us before using.

Treatment and purification as above. Ethyl-anhydracetonebenzil is deposited from alcohol in colourless minute needles, melting at 156°.

	Substance.	CO_2.	H_2O.
I	0·1922	0·5773	0·1147
II	0·1881	0·5637	0·1127

	Calculated for $C_{19}H_{18}O_2$.		Found.	
			I.	II.
C_{19}	228	82·01	81·91	81·72
H_{18}	18	6·48	6·63	6·66
O_2	32	11·51	—	—
	278	100·00		

Amyl-anhydracetonebenzil, $C_{22}H_{24}O_2$.

Benzil	60 grams.
Methyl hexyl ketone*	40 „
Caustic potash solution (sp. gr. 1·27) ..	10 c.c.

Treatment and purification as above. Amyl-anhydracetonebenzil crystallises from hot alcohol in tufts of colourless slender silky needles, melting at 150·5°.

	Substance.	CO_2.	H_2O.
I	0·1981	0·5964	0·1334
II	0·1645	0·4948	0·1103

	Calculated for $C_{22}H_{24}O_2$.		Found.	
			I.	II.
C_{22}	264	82·50	82·11	82·03
H_{24}	24	7·50	7·48	7·45
O_2	32	10·00	—	—
	320	100·00		

Normal School of Science,
South Kensington.

---

* Prepared by Kahlbaum by distilling castor-oil with caustic potash, and purifying the compound by means of hydrogen sodium sulphite.

XLVI.—*Researches on the Constitution of Azo- and Diazo-derivatives.* II. *Diazoamido-compounds* (continued).

By Raphael Meldola, F.R.S., Professor of Chemistry, and F. W. Streatfeild, Demonstrator of Chemistry in the Finsbury Technical College, City and Guilds of London Institute.

It was shown in our last communication on this subject (this vol., p. 102), that when diazotised paranitraniline acts on metanitraniline or diazotised metanitraniline on paranitraniline, a compound is obtained which, according to its mode of formation, might be written:—

$$\underset{(1)}{NO_2}\cdot C_6H_4\cdot\underset{(3)}{N_2}\cdot\underset{(4)}{NH}\cdot C_6H_4\cdot\underset{(1)}{NO_2},\ \text{or}\ \underset{(1)}{NO_2}\cdot C_6H_4\cdot\underset{(4)}{N_2}\cdot\underset{(3)}{NH}\cdot C_6H_4\cdot\underset{(1)}{NO_2}.$$

Reasons were given in the paper referred to for regarding the last formula as that which actually expresses the constitution of the compound in question, the inference from this conclusion being that in the first mode of preparation isomeric transformation takes place, possibly through the formation of an intermediate additive compound.

Among the facts previously made known to the Society, one of the most interesting appeared to be the decomposition of this unsymmetrical compound (m. p. 211°), by means of hydrochloric acid, into a *mixture* of meta- and para-nitranilines and the two corresponding nitrochlorobenzenes. This decomposition takes place completely and rapidly in a sealed tube at 100°, or more slowly, but with precisely the same results, on simply heating for some time with the strong acid in an open vessel. This discovery certainly stands opposed to the general belief that the action of acids on diazoamido-compounds is in the first place simply a resolution of the compound into its constituents, viz., the diazo-chloride and amine, and that these are then decomposed according to the equations—

$$X\cdot N_2\cdot NH\cdot Y + HCl = X\cdot N_2\cdot Cl + Y\cdot NH_2 \ldots\ldots\ldots\ldots\ldots (I)$$

$$X\cdot N_2\cdot Cl = X\cdot Cl + N_2, \text{ or } X\cdot N_2\cdot Cl + OH_2 = X\cdot OH + N_2 + HCl \ldots\ldots\ldots\ldots (II)$$

If the decomposition of diazoamido-compounds by acids were of this simple character, the unsymmetrical compound should have given but one nitrochlorobenzene and one nitraniline, unless we suppose that the diazo-chloride and amine react when heated together in some manner at present unknown. If this reaction between the diazo-chloride and amine (nitraniline) be not that of the formation of an intermediate compound which immediately undergoes decomposition, it must be supposed that an interchange of the groups $—N_2·Cl$ and NH_2 in two distinct molecules takes place, a belief for which there is at present no warrant. We may here state that we have repeated the experiments on the decomposition of the nitrodiazobenzene chlorides in the presence of dissimilar nitranilines, as described in our last paper (*loc. cit.*, p. 106), using an open vessel instead of a sealed tube, but the evidence of the formation of mixed products is in this case by no means so satisfactory as when sealed tubes are employed, the unsatisfactory results being no doubt due to the gradual weakening of the hydrochloric acid on boiling, and the consequent formation of phenolic products. It must be understood that this observation does not apply to the decomposition of the unsymmetrical dinitrodiazoamido-compound in an open vessel, as in this case the products, as already stated, are identical with those obtained in a sealed tube, viz., the *mixed* nitranilines and nitrochlorobenzenes.

The evidence thus far obtained points to the conclusion that the action of acids on diazoamido-compounds is by no means so simple as is represented in the last equations, a conclusion which is considerably strengthened by the circumstance that the ethyl-derivative of the unsymmetrical compound also gives a *mixture* of ethylnitranilines and nitrochlorobenzenes on decomposition by hydrogen chloride. As mentioned in our last paper, these results are in complete accordance with those obtained by other investigators who have studied the decomposition of mixed diazoamido-compounds. Thus, the compound obtained by the action of diazotised aniline on amidobenzoic acid, or of diazobenzoic acid on aniline, when decomposed by hydrochloric acid, gives a mixture of aniline, phenol, amidobenzoic acid, and hydroxybenzoic acid (Griess, *Ber.*, 1874, 1619).* So also the compound obtained by the action of diazotised aniline on paratoluidine, or of diazotised paratoluidine on aniline gives on decomposition a mixture of paratoluidine, aniline, paracresol, and phenol (Nölting and Binder, *Bull. Soc. Chim.*, **42**, 336). It is certainly a fact of the greatest interest, and one of which the complete significance cannot at present be perceived, that an unsymmetrical compound formed by the action of $X·N_2—$ on $Y·NH_2$ can also be produced by the action of $Y·N_2—$ on $X·NH_2$, and that this compound when decomposed by acids should split up *as though both isomerides*, $X·N_2·NH·Y$ and $Y·N_2·NH·X$, *were present.*

We may here point out that the less acid and more unstable diazoamido-compounds, such as $C_7H_7{\cdot}N_3H{\cdot}C_6H_5$, &c., are far less satisfactory to work with than the more distinctly acid dinitro-derivatives, not only on account of the greater stability of the latter, but also because of their easier preparation, and still more because of the very definite and easily recognizable products which they give on decomposition.* These advantages render the dinitrodiazoamido-compounds particularly well suited for a series of investigations such as those on which we are at present engaged, and we propose to continue our work with these compounds in the hope that the information derived from a study of their reactions and properties will afterwards enable us to return with new light to the question of the constitution of the simpler diazoamido-compounds.

---

* According to Griess, chlorobenzoic acid is also formed, but this is doubtless due to the same reaction as that which results in the formation of hydroxybenzoic acid, viz., the decomposition of the diazobenzoic acid produced by the resolution of the compound by the hydrochloric acid.

I. *Decomposition of Dinitrodiazoamido-compounds by cold Hydrochloric Acid.*

It has long been known that diazoamido-compounds immediately begin to decompose in the presence of acids, even in the cold, the rate of decomposition depending on the stability of the compound, the strength of acid, &c. Thus it has been shown by O. N. Witt (*Ber.*, 1877, 1309) that it is only necessary to add acetic acid to a mixed solution of diazoamidobenzene and metaphenylenediamine in alcohol to obtain an immediate formation of chrysoidine.† The dinitro-derivatives which form the subject of the present investigation are no exception to this rule; when left in contact with strong hydrochloric acid at ordinary temperatures, they gradually dissolve with the formation of very definite products. Unlike the simpler members of the group, such as diazoamidobenzene, these compounds decompose without the formation of phenols or tarry products, or conversion into amidoazo-compounds, so that a study of this reaction promised to furnish important information with respect to the present inquiry. Some preliminary experiments served to show that the clear acid solution contained the materials capable of reproducing the dinitrodiazoamido-compound, presumably the nitrodiazo-chloride and nitraniline, since it was only necessary to dilute the solution with water and replace the excess of hydrochloric by acetic acid by the addition of sodium acetate to obtain the original dinitrodiazoamido-compound. According to the prevailing view of this decomposition, we should thus have in solution, in the case of the symmetrical dipara-compound, paranitraniline and paranitrodiazobenzene-chloride:—

---

* The facility with which the symmetrical dipara- and dimeta-compounds break up into the nitrochlorobenzenes, when heated with hydrochloric acid, suggests the employment of these compounds for the preparation of the nitrofluorbenzenes instead of the benzenediazopiperidine recently made use of by Wallach (*Ann.*, 235, 255) for this purpose. The dinitrodiazoamido-compounds offer obvious economical

† In order to get this reaction with the more stable dinitrodiazoamido-compounds at present under consideration, it is necessary to add hydrochloric acid to the alcoholic solution, and warm gently.

$$\underset{(1)}{NO_2}\cdot C_6H_4\cdot \underset{(4)}{N_2}\cdot \underset{(4)}{NH}\cdot C_6H_4\cdot \underset{(1)}{NO_2} + HCl = \underset{(1)}{NO_2}\cdot C_6H_4\cdot \underset{(4)}{N_2Cl} + \underset{(4)}{NH_2}\cdot C_6H_4\cdot \underset{(1)}{NO_2}.$$

But in this case, as in that of the decomposition by hot acid, the symmetry of the two halves of the molecule renders it impossible to decide whether the course of the reaction is really so simple as above represented. Two preliminary experiments made with the unsymmetrical compound (m. p. 211°) and its ethyl-derivative (m. p. 148°) appeared to indicate that, even in the cold, the decomposition products were of a mixed character, and that this decomposition would therefore require special investigation:—

(1.) Some of the unsymmetrical compound was allowed to stand for two days in contact with a large excess of strong hydrochloric acid. The solution was then filtered in order to remove a slight residue of apparently unaltered substance, and the filtrate mixed with a solution of platinic chloride, when orange needles immediately began to separate. After remaining for some hours, the crystalline deposit was collected, washed with hydrochloric acid, then with water and finally with alcohol. A determination of platinum in a specimen of the dry salt gave the following results:—

0·1308 gram gave 0·0358 gram Pt .... = 27·37 p. c.
Theory for $(NO_2\cdot C_6H_4\cdot N_2Cl)_2,PtCl_4$ .... = 27·52 „

The salt was consequently a platinochloride of nitrodiazobenzene, and in order to determine which modification, or whether it was a mixture that we had in hand, it became necessary to decompose the compound so as to obtain the nitrochlorobenzene. It was found that this decomposition took place quantitatively on simply boiling the salt with water, when nitrochlorobenzene distilled over with the steam. The white crystalline distillate, after being allowed to dry, had the melting point of pure metanitrochlorobenzene.

This experiment showed, therefore, the presence of metanitrodiazobenzene-chloride in the solution, and it might have been inferred therefrom that the constitution of the unsymmetrical compound was $\underset{(1)}{NO_2}\cdot C_6H_4\cdot \underset{(3)}{N_2}\cdot \underset{(4)}{NH}\cdot C_6H_4\cdot \underset{(1)}{NO_2}$. But this conclusion is at variance with that suggested in our last paper, and it did not follow that the presence of *para*nitrodiazobenzene-chloride had been disproved, since the platinic chloride may simply have effected a fractional separation of the two diazo-chlorides, or the *meta*-chloride only may have been capable of forming a double salt.

In order to test this last conclusion, a mixture of equal weights of paranitraniline and metanitraniline was diazotised in hydrochloric acid in the usual way, and platinic chloride added to the solution. The orange crystalline precipitate was collected, washed, and then decomposed by boiling with water. The distillate consisted of pure metanitrochlorobenzene, thus proving that paranitrodiazobenzene is incapable of forming a platinochloride,* and at the same time showing that this modification may have been present among the decomposition products of the unsymmetrical compound.

(2.) Some of the ethyl-derivative of the unsymmetrical compound was allowed to stand for two to three hours at the ordinary temperature in contact with a large excess of hydrochloric acid. The solution was then filtered in order to remove a slight residue, and sodium nitrite added to the filtrate, when a white crystalline precipitate at once separated. The precipitate, after being collected, washed, and dried, proved to be a mixture of the nitrosamines of ethylparanitraniline and ethylmetanitraniline.

These two experiments taken together appeared to indicate that the unsymmetrical compound and its ethyl-derivative split up under the influence of cold hydrochloric acid with the formation of the same mixed products as when hot acid is employed. In order to submit this reaction to systematic examination, we had, therefore, to devise some ready method by which the diazo-chlorides and nitranilines or ethylnitranilines could be separated and identified. The following process has answered all requirements, and has been used throughout the series of experiments detailed below:—

The cold hydrochloric acid solution containing the diazo-chlorides and nitranilines or ethylnitranilines is gradually dropped with constant cooling into an alkaline solution containing the necessary quantity of β-naphthol calculated for the weight of dinitrodiazo-compound employed. The diazo-chlorides and nitranilines or ethylnitranilines are all precipitated together, the former in the form of azo-β-naphthol-compounds, and the latter as free bases. From the mixed precipitate, after collecting and washing, hydrochloric acid dissolves out the nitranilines or ethylnitranilines, which can be identified by the usual methods, and the nitrobenzeneazo-β-naphthols are then left in a state of purity, and can be similarly identified. The advantages of this method are sufficiently obvious: all the products of decomposition are thrown down in an easily recognisable form at one operation, and the possibility of complication by the action of heat is avoided. Thus, in the case of an ethyl-derivative the reactions might be represented as follows:—

---

* This was confirmed by direct experiment, a solution of paranitrodiazobenzene chloride giving no precipitate with platinic chloride.

$$\text{(I)}\ldots\quad NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2 + 2HCl = NO_2{\cdot}C_6H_4{\cdot}N_2Cl + NO_2{\cdot}C_6H_4{\cdot}N(C_2H_5)H,HCl.$$

$$\text{(II)}\ldots\quad NO_2{\cdot}C_6H_4{\cdot}N_2Cl + NO_2{\cdot}C_6H_4{\cdot}(C_2H_5)H,HCl + NaOH + C_{10}H_7{\cdot}ONa = NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH^* + NO_2{\cdot}C_6H_4{\cdot}N(C_2H_5)H + 2NaCl + OH_2.$$

We now proceed to give the results of the application of this method to the various compounds described in our last paper.

1. *Decomposition of the Symmetrical Dipara-compound, m. p.* 223°.

One gram of the above substance was allowed to stand for about 24 hours at the ordinary temperature, in contact with a considerable excess of strong hydrochloric acid, by which time the substance had nearly all dissolved. The residue was filtered off, washed with water, crystallised from alcohol, and its melting point taken; this, together with the other properties, showed that the insoluble portion was simply some of the original substance remaining unacted on owing to an insufficiency of acid. The hydrochloric acid solution was then dropped into an alkaline solution of β-naphthol in the manner above described. The red precipitate was collected, washed with cold water, and then extracted with hot dilute hydrochloric acid; the acid filtrate, on the addition of a slight excess of caustic soda, gave a yellow crystalline precipitate, which was identified as pure paranitraniline (m. p. 146°). The red azo-compound was crystallised from glacial acetic acid, and identified as paranitrobenzeneazo-β-naphthol (m. p. 249°, Meldola, Trans., 1885, 662).

This experiment shows, therefore, that the products of decomposition are paranitrodiazobenzene-chloride and paranitraniline.

2. *Decomposition of the Unsymmetrical Compound, m. p.* 211°.

The foregoing experiment was repeated with every possible precaution on the above compound, and in order to give completeness to the result two preparations were employed, one obtained by the action of diazotised paranitraniline on metanitraniline, and the other prepared by the reverse method. The products of decomposition *were the same in both cases*, thus giving additional evidence of the identity of the two compounds. The very slight insoluble residue proved in both cases to be simply unaltered substance, a fact of some importance in the present experiment, since it shows, as we have frequently established by fractional crystallisation from alcohol, that this unsymmetrical modification is a distinct chemical substance,* and that the acid does not effect a fractional separation into different compounds. The details of the experiment are as follows:—

---

* This formula is assumed provisionally. See Trans., 1885, 662, foot-note.

The red azo-precipitate was collected and washed as usual, then boiled with dilute hydrochloric acid and filtered. In order to make sure that the whole of the nitranilines were obtained, the alkaline filtrate from the azo-compound was acidified with hydrochloric acid, mixed with the acid filtrate from the azo-compound, and the whole concentrated by evaporation to a small bulk. After being allowed to cool, the acid liquor was filtered, in order to remove common salt, and the nitranilines thrown out by caustic soda, collected, and washed with cold water. A specimen of the crystalline precipitate, on reduction and oxidation, gave the indamine reaction most intensely, and this, together with the vague melting point (101—121°), left no doubt that we had a mixture of the two nitranilines. Additional confirmation was obtained by fractionally crystallising the nitranilines from water. The first crop of crystals melted at 138—145·5°; the second at 94—104°; and the mother-liquor from the latter on reduction gave abundant evidence of the presence of metaphenylenediamine on applying the nitrous acid test. The azonaphthol-compound, after crystallisation from acetic acid, was identified as a mixture of para- and meta-nitrobenzeneazo-β-naphthol (Meldola, Trans., 1885, 668).†

From this experiment, it follows that cold hydrochloric acid decomposes the unsymmetrical compound into *a mixture of para- and meta-nitrodiazobenzene-chlorides and para- and meta-nitraniline.*

Decomposition and Recomposition of the foregoing Compound.—As a result of the last experiment it seemed probable that if the dinitrodiazoamido-compound potentially present in the acid solution were thrown out by the dilution of the latter, the precipitate would not consist of the original compound, but of a mixture of the isomeric modifications, since the two nitranilines and the two nitrochlorobenzenes had been proved to be present. In order to submit this deduction to experimental proof, some of the unsymmetrical compound was decomposed by cold hydrochloric acid in the manner described, and the solution after filtration diluted with water, and partially neutralised by ammonium carbonate. After standing for some hours, the bulky yellow precipitate was collected, washed with water, and dried. The substance then melted at 195—201°. After one crystallisation from alcohol, the melting point was 202—203°; after a second crystallisation, the melting point was 209—209.5°, and then remained constant. As far as this experiment goes, it appears, therefore, that the precipitate obtained on recombination of the decomposition products of the unsymmetrical compound is a mixture, and not one definite dinitrodiazoamido-compound.

---

* If the unsymmetrical modification had been a molecular compound of the other two modifications, it would have been possible to prepare it by crystallising a mixture of the dipara- and dimeta-compounds. This experiment was tried by dissolving equal weights of these two last compounds in boiling alcohol and allowing the solution to cool. The two substances, however, separated out in their distinctive crystalline forms, and could be easily separated, nothing of the character of a molecular compound having been produced. This unsymmetrical compound is, moreover, the complete analogue of such mixed diazoamido-compounds as $C_6H_5 \cdot N_3H \cdot C_7H_7$, which it resembles in all its modes of decomposition. The possibility of the latter being a molecular compound of its two isomerides, $C_6H_5 \cdot N_2 \cdot NH \cdot C_7H_7$ and $C_7H_7 \cdot N_2 \cdot NH \cdot C_6H_5$, cannot be entertained.

† I will take the present opportunity of correcting the melting point of this last compound to 193—194° instead of 191—192°, as given in the paper above referred to.—R. M.

3. *Decomposition of the Symmetrical Dimeta-compound, m. p.* 194°.

This substance dissolved in the cold acid with only a very slight residue, which was too small to attempt to purify by crystallisation. Its melting point was 170—178°, and it most probably consisted of Hallmann's dinitroamidoazo-compound mixed with impurities. The acid filtrate, on being mixed with the alkaline solution of β-naphthol, gave a red azo-compound, which was collected, washed, extracted with hot dilute hydrochloric acid, dried, and crystallised from acetic acid; it then formed splendid red needles melting at 193—194°, and thus proving to be metanitrobenzeneazo-β-naphthol. The acid extract on concentration and neutralisation, gave pure metanitraniline (m. p. 112°); a specimen on reduction and oxidation gave no indication of the indamine reaction.

The above compound is thus resolved by hydrochloric acid into metanitraniline and metanitrodiazobenzene-chloride.

4. *Decomposition of the Ethyl-derivative of the Symmetrical Dimeta-compound, m. p.* 119°.

This compound dissolves in the acid, with practically no residue. The azo-precipitate proved to be metanitrobenzeneazo-β-naphthol (m. p. 193—194°), and the acid extract, on treatment in the usual way, was found to contain ethylmetanitraniline. The latter was identified by reduction and the nitrous acid test, which gave ethylchrysoidine, and also by conversion into the nitrosamine, which, after crystallisation from dilute alcohol, had a melting point of 41—42°.*

---

* Nölting and Stricker give the melting point of this compound as 47°. Our preparations have, however, always had the above melting point, and it is probable that the temperature given by these authors is due to a misprint (*Ber.*, 1886, 540).

The products of decomposition are, therefore, in this case metanitrodiazobenzene-chloride and ethylmetanitraniline.

5. *Decomposition of the Ethyl-derivative of the Unsymmetrical Compound, m. p.* 148°.

One gram of a pure crystalline preparation was decomposed in the usual way, a slight residue of unaltered substance being removed by filtration. The reddish-brown azonaphthol precipitate, after being submitted to the usual treatment and crystallised from glacial acetic acid, proved to be a mixture of meta- and para-nitrobenzeneazo-β-naphthol. The acid extract containing the ethylnitranilines gave the indamine reaction most intensely on reduction and oxidation, the solution rapidly becoming deep violet on exposure to the air. The addition of sodium nitrite to the acid solution caused the precipitation of a nitrosamine which, after crystallisation from dilute alcohol, proved to be a mixture of ethylpara- and ethylmeta-nitrophenylnitrosamine.

The products of decomposition of this ethyl-derivative are therefore analogous to those of the substance from which it is derived, viz., *a mixture of the two nitrodiazobenzene-chlorides and the two ethyl nitranilines.*

6. *Decomposition of the Ethyl-derivative of the Symmetrical Diparacompound, m. p.* 191—192°.

The red azo-precipitate, after crystallisation from acetic acid, had a melting point of 249—250°; the nitrosamine melted at 119—120°.

The products of decomposition are in this case, therefore, paranitrodiazobenzene-chloride and ethylparanitraniline.

7. *Decomposition of the Ethyl-derivative, m. p.* 174—175°, *obtained by the action of diazotised Metanitraniline on Ethylparanitraniline.*

In accordance with the results obtained by the action of hot hydrochloric acid on this substance (Trans., 1887, 110), it might have been expected that the products of decomposition would be ethylparanitraniline and metanitrodiazobenzene-chloride. Experiment proved this to be the case, the azonaphthol-compound melting at 193—194°, and the nitrosamine at 119·5°. The acid extract, on reduction and oxidation, gave no indication of the formation of indamine.

8. *Decomposition of the Ethyl-derivative, m. p.* 187°, *obtained by the action of diazotised Paranitraniline on Ethylmetanitraniline.*

As in our last paper we stated that we had reason to suspect that this substance might be an amidoazo-compound, its decomposition by cold hydrochloric acid was studied with special interest, and every precaution was taken to insure the purity of the specimen employed. One gram, in a very fine state of division, was mixed in the usual way with excess of strong acid and allowed to stand, with occasional agitation, for about an hour, by which time practically the whole of the substance had dissolved, the solution being only slightly turbid. After filtration and precipitation by the alkaline solution of β-naphthol, in the manner described, the acid extract from the azonaphthol-compound was concentrated by evaporation, and then tested by reduction and oxidation, but gave no trace of coloration. With sodium nitrite, this reduced solution gave a copious brown precipitate (ethylchrysoïdine), indicating the presence of ethylmetaphenylenediamine. The remainder of the acid (unreduced) solution gave an oily nitrosamine on treatment with sodium nitrite, which soon solidified, and after crystallisation from dilute alcohol had a melting point of 41°. The azonaphthol-compound in the crude state melted at 248°, and after crystallisation from acetic acid, at 249—250°.

The products of decomposition are in this case, therefore, ethylmetanitraniline and paranitrodiazobenzene-chloride. The facility with which this compound is decomposed, taken in conjunction with the nature of the products, is thus opposed to the view which we had taken at first, and the present compound, when decomposed by cold hydrochloric acid, agrees completely in its behaviour with that of the true diazoamido-compounds previously described.

II. *Further Examination of the Ethyl-derivative, m. p.* 187°.

Our first impressions with respect to the nature of this compound having been negatived by the last experiment, it became necessary to submit the substance to a more searching investigation, since the existence of *three* isomeric unsymmetrical dinitrodiazoethylamido-compounds is completely opposed to the generally received view of the constitution of these compounds; moreover, with the establishment of this fact, Kekulé's formula, as will be shown subsequently, becomes no longer tenable.

A specimen of the substance carefully purified by crystallisation from alcohol, gave the following results on analysis:—

I. 0·2328 gram gave 0·4525 gram CO_2 and 0·0875 gram H_2O.
II. 0·1863 „ „ 0·3610 „ „ 0·0698 „ „
III. 0·1058 „ burnt in a vacuum with CuO, gave 19·6 c.c. N. at 10° and 765 mm. bar.

	Calculated for $NO_2\cdot C_6H_4\cdot N_3(C_2H_5)\cdot C_6H_4\cdot NO_2$.	Found. I.	Found. II.	Found. III.
C	53·33	53·01	52·84	—
H	4·12	4·17	4·16	—
N	22·22	—	—	22·32

Decomposition by Hot Hydrochloric Acid.—On boiling the substance with strong acid in a flask, it is decomposed quantitatively into paranitrochlorobenzene (m. p. 83°) and ethylmetanitraniline (m. p. of nitrosamine 41°). No tarry products are formed in this reaction.

Products of complete Reduction.—On the supposition that the substance was an amidoazo-compound of the formula suggested in our last paper (this vol., p. 111), it might have been expected to yield on reduction paraphenylenediamine and the unsymmetrical ethyltriamidobenzene, $C_6H_3(NH_2)_2\cdot NH\cdot C_2H_5 = 1 : 2 : 4$. The latter compound, containing two NH_2-groups in the ortho-position, could have been identified by its furnishing an azine on condensation with double ketones. In order to test this point, some of the ethyl-derivative was dissolved in glacial acetic acid, and reduced by zinc-dust; the solution was then filtered and mixed with a 1 per cent. solution of phenanthraquinone in acetic acid. No formation of azine was observed, even after warming the mixed solutions for some hours.

The absence of the unsymmetrical ethyltriamidobenzene having been proved by the last experiment, a further quantity of the substance was completely reduced by boiling the alcoholic solution with tin and hydrochloric acid. The alcohol was distilled off, the solution diluted with water, and the tin removed as sulphide. The solution containing the hydrochlorides of the bases was then evaporated to dryness, and a portion of the residue boiled for some hours with an excess of glacial acetic acid and anhydrous sodium acetate, with the addition of some acetic anhydride. On diluting with water and allowing it to stand, a flocculent acetyl-derivative, contaminated with colouring matter, gradually separated. After purification by several crystallisations from glacial acetic acid, this substance was identified as the diacetyl-derivative of paraphenylenediamine. The remaining portion of the hydrochlorides of the bases was dissolved in water, and sodium nitrite added. A copious precipitate of a brown colouring matter, resembling ordinary "Bismarck brown" in its characters, sufficiently indicated the presence of a *meta*diamine or ethyldiamine. The products of complete reduction appear, therefore, to be paraphenylenediamine and ethylmetaphenylenediamine, a result which finds confirmation in the fact that these products give the indamine reaction most intensely on joint oxidation (this vol., p. 112). It is true that the colour thus developed is more violet in shade than that produced by the oxidation of the products of reduction of the 174—175° m. p. isomeride, but this is doubtless due to the isomerism of the respective indamines, the one being formed by the oxidation of a mixture of paraphenylenediamine with ethylmetaphenylenediamine, and the other being produced by the oxidation of a mixture of metaphenylenediamine with ethylparaphenylenediamine. We have satisfied ourselves by the oxidation of prepared mixtures of the diamines and ethyldiamines that such a difference of colour does exist in the two cases. From these results, it appears, therefore, that the ethylderivative, melting at 187°, is a true diazoamido-compound, or at any rate that it behaves as such towards every reagent that has been tried.

III. *Salts of Dinitrodiazoamido-compounds.*

The dinitrodiazoamido-compounds, and especially that modification derived from paranitraniline, are distinct acids forming well-defined crystalline salts with certain metals. We determined therefore to take advantage of this property, and to examine as many of these salts as could be prepared in a state of purity, in order to ascertain if possible the basicity of the acids. Many practical difficulties have presented themselves in the course of this branch of the work, but the general result indicates with sufficient distinctness that only 1 atom of displaceable hydrogen is present in these compounds. The difficulties have arisen in the first place from the necessarily restricted choice of metals, because only the alkaline salts of the diazo-compounds are available for the purpose of double decomposition, and these being but sparingly soluble in water, alcohol must of necessity be used as a solvent. Then again it was found that the salts of the heavy metals could only be formed in the presence of excess of alkali, so that our selection was limited to those metals whose oxides or hydroxides were soluble in alkali. The salts are also in most cases explosive, and thus require special treatment in order to get trustworthy results on analysis. With the exception of those of the alkaline metals, all the salts are insoluble in water or alcohol, and are thus incapable of being further purified when once formed. Of the salts formed by the heavy metals, only those of cadmium, cobalt, and nickel are crystalline, and the difficulty of obtaining these in a state of purity is much enhanced by a tendency which they have to form basic compounds containing an excess of the metal. The details of the mode of preparation and analysis are briefly given below, the three dinitrodiazo-compounds being spoken of for brevity as the dipara-, the unsymmetrical, and the dimeta-compounds.

The *potassium* and *sodium salts* of the dipara-compound can be best obtained by dissolving the acid in warm alcohol with the addition of an excess of an aqueous solution of the alkali, and then diluting with warm water. The salts are deposited, on cooling, in the form of large needles having a bright bluish metallic reflex, but these are stable only in the presence of excess of alkali, and could not therefore be analysed. These salts are decomposed on washing with water; the excess of potash or soda can, however, be removed by washing with ammonia solution, but the salts cannot be dried without undergoing decomposition by the carbonic acid of the atmosphere. The corresponding salts of the unsymmetrical and the dimeta-compounds are less stable than those of the dipara-compound, and no attempt was therefore made to isolate them. Attempts to prepare a *lithium salt* of the dipara-compound were unsuccessful.

The *silver salt* of the dipara-compound separates as a bright-red amorphous powder on adding an ammoniacal solution of silver nitrate to a solution of the substance in alcoholic ammonia. The dry salt explodes on heating, and it was therefore found necessary for the purposes of analysis to decompose a weighed quantity of the salt by allowing it to stand for some time under rather strong nitric acid. The free diazo-compound was then filtered off, the residue washed, and the silver in the filtrate precipitated as chloride. The results obtained, although the analysis was several times repeated with different preparations, did not agree very exactly either among themselves or with the calculated amount of silver, but the numbers fairly approximated to those required by the formula

$$NO_2\cdot C_6H_4\cdot N_2\cdot NAg\cdot C_6H_4\cdot NO_2,$$

leaving no doubt in our minds that the acid is monobasic. An attempt was made to confirm this result by a volumetric method. For this purpose a decinormal solution of ammoniacal silver nitrate was prepared, and a known weight of the dipara-compound, dissolved in alcohol and ammonia, was then titrated by means of the silver solution. The red colour of the precipitate interferes with the sharpness of the result, and it was very difficult to determine the exact point of complete precipitation, that is, the point when the red colour of the alcoholic solution of the ammonium salt had just disappeared. In this case, the results also distinctly indicated that the acid was monobasic. The silver salts of the unsymmetrical and dimeta-compounds did not appear sufficiently promising to attempt their analysis. The latter is precipitated as a brown jelly on adding the ammoniacal silver solution to the alcoholic solution of the sodium salt of the dimeta-compound.*

---

* This compound being much less acid than its isomerides does not form an ammonium salt.

The *copper salts* of the three compounds are very definite in appearance, but presented the usual difficulties of purification and analysis. The gradation of colour is very noticeable in these salts, that of the dipara-compound being chocolate-brown, the dimeta-compound light ochreous, and the unsymmetrical compound of an intermediate colour. The salts are all amorphous insoluble powders which readily deflagrate on heating. The dipara-salt was prepared by precipitating an ammoniacal solution of the substance in alcohol with a solution of ammonio-cupric sulphate. The precipitate was collected, washed thoroughly with alcohol, then with dilute ammonia, and finally with water, and dried. Gravimetric and volumetric analyses of the salt gave results approximating to the formula $(NO_2\cdot C_6H_4\cdot N_3\cdot C_6H_4\cdot NO_2)_2Cu$.

The best method of decomposing the copper salts was found to be that of heating first with a few drops of sulphuric acid (strong acid and water in equal parts) in an open dish on a water-bath till the decomposition of the substance was complete, and then drying down at a higher temperature till the residue was carbonised and the excess of acid removed by ignition. The copper was extracted from the residue by means of dilute nitric acid, and determined as oxide by the usual methods. The most satisfactory numerical results were obtained on analysis of the copper salt of the unsymmetrical compound by the foregoing method:—

0·3585 gram gave 0·0438 CuO = 9·75 p. c. Cu.
Calculated .... 9·45 „

This result was confirmed by titration with a standard solution prepared by dissolving pure (electrolytic) copper in nitric acid and adding excess of ammonia, and then diluting to decinormal strength (1 c.c. = 0·00316 Cu).

0·0953 gram of the substance dissolved in alcohol and ammonia required 2·9 c.c. of the copper solution for complete precipitation = 0·00916 gram Cu. The theoretical quantity required by the formula is 0·01054 gram Cu.

The error here is no doubt due, as in the case of the silver salt, to the extreme difficulty of fixing the exact point of complete precipitation.

The analysis of the dimeta-copper salt also gave results fairly approximating to those required by the foregoing formula.

The *cadmium salt* of the dipara-compound was prepared by adding an ammoniacal solution of cadmium chloride to the hot alcoholic (ammoniacal) solution of the substance. The salt separates out on cooling in the form of scaly crystals which glisten in the solution with a steel-blue lustre and become bright-red on drying. The dry salt explodes somewhat sharply when heated, leaving a woolly carbonaceous residue. The following results were obtained on analysis:—

I. 0·2983 gram decomposed by ignition with H_2SO_4 gave 0·0631 gram CdS.

II. 0·0820 gram moistened with H_2SO_4 and burnt in a porcelain boat in the presence of lead chromate, gave 0·1260 gram CO_2 and 0·0246 gram $CdSO_4$.

III. 0·1158 gram burnt in a vacuum with CuO gave 20·5 c.c. N at 10° and 756 mm. bar.

	Calculated for $(NO_2\cdot C_6H_4\cdot N_3\cdot C_6H_4\cdot NO)_2Cd$.	Found.		
		I.	II.	III.
Cd......	16·37	16·53	16·15	—
C	42·10	—	41·90	—
N	20·47	—	—	21·08*

The *cobalt salt* of the dipara-compound was prepared by adding an ammoniacal solution of cobalt nitrate to a hot alcoholic solution of the ammonium salt of the substance. The salt separates out on cooling in the form of scaly crystals which glisten in the solution with a steel-blue lustre and acquire a coppery appearance on drying. The salt was analysed by decomposition with sulphuric acid, as in the case of the copper and cadmium salts, the cobalt being weighed as sulphate:—

0·1777 gram gave 0·0464 gram $CoSO_4$ = 9·20 per cent. Co.

A salt of the formula $(NO_2\cdot C_6H_4\cdot N_3\cdot C_6H_4\cdot NO_2)_2Co$ requires 9·29 per cent. of Co.

The cobalt salts of the other modifications could not be prepared sufficiently pure for analysis.

The *nickel salt* of the dipara-compound was prepared in the same manner as the cobalt salt. It separates from the solution much less readily than this last salt, and is less distinctly crystalline. It appears in the solution in the form of small steel-blue scales, which become dull coppery on drying. The analytical results showed the salt to be impure, and its further examination was therefore abandoned.

IV. *Theoretical bearing of the results on existing views of the Constitution of the Diazoamido-compounds.* By R. Meldola.

The most important fact arising out of the present series of experiments is undoubtedly, from a theoretical point of view, the existence of *three* isomeric ethyl-derivatives containing para- and meta-nitraniline residues. Expressing these residues by the symbols P and M, it is obvious that Kekulé's formula only admits of the two modifications—

---

* Great difficulty has been experienced in getting good results for the N in the analysis of this and other salts. Numerous determinations have been made by Mr. H. C. Coram, Storekeeper of the Chemical Department, to whom we take the present opportunity of expressing our thanks for the assistance which he has given in the course of the work.

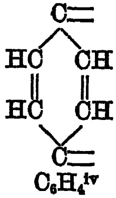
$$P{\cdot}N_2{\cdot}N(C_2H_5){\cdot}M \text{ and } M{\cdot}N_2{\cdot}N(C_2H_5){\cdot}P.$$

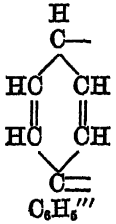
If we suppose that the first of these compounds (m. p. 187°) is the one produced by the action of diazotised paranitraniline on ethyl-*m*-nitraniline, and that the second (m. p. 174—175°) is the one produced by the action of diazotised metanitraniline on ethyl-*p*-nitraniline, there then remains no other formula for the ethyl-derivative of m. p. 148° prepared by the direct ethylation of the unsymmetrical compound. It is obvious, therefore, that the commonly accepted formula is inadequate to express these facts, and this circumstance, combined with the failure of this formula to account for the formation of mixed products by the decomposition of the unsymmetrical compound and its ethyl derivative without the assumption of continual intramolecular rearrangement (see this vol., p. 116), seems to necessitate a rediscussion of the whole question of the constitution of the diazo-amido-compounds. As long as the 187° m. p. modification was thought to be an amidoazo-compound we had only two ethyl-derivatives to consider, and no difficulty then stood in the way of accepting Kekulé's formula. In our last paper it was shown that this formula could be applied with considerable success to explain the behaviour of the dinitro-diazo-amido-compounds by the use of Victor Meyer's supplementary hypothesis of the formation of intermediate additive compounds. But the undoubted fact that the ethyl-derivative melting at 187° is a true diazo-amido-compound gives a new aspect to the case, and our views concerning the constitution of the diazo-amido-compounds must accordingly undergo revision.

In face of the difficulties which have hitherto been encountered in all attempts to find a truly satisfactory formula for these compounds, I do not now propose to do more than put forward a very brief sketch of the views which I have formed on this question, reserving the full elaboration of these views till further insight has been gained by means of a more extended series of experiments.* It will suffice at present to express my conviction that the final solution of the problem will be arrived at by regarding phenyl as a triatomic instead of a monatomic radicle, as has always hitherto been the case. This view is in harmony with the double ketone theory of the constitution of quinone, according to which phenylene is a tetratomic radicle:—

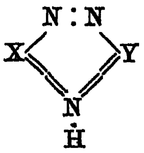
---

* A more detailed theoretical discussion of the proposed formulæ will be found in a paper which I have communicated to the *Philosophical Magazine*, and which will appear in the June number of that publication.

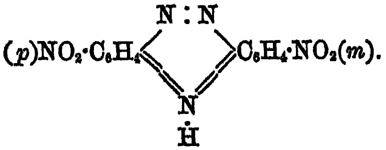




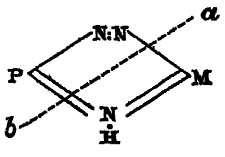
* By adopting this view, it becomes possible to construct a formula which accords well with all the known characters of the diazoamido-compounds, or at any rate of those compounds containing dissimilar radicles, such as the unsymmetrical compound of m. p. 211° described in our previous paper (this vol., pp. 102 and 109). The generalised formula in question is thus written:—

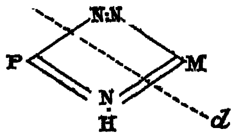


Applying this to the unsymmetrical compound it will be seen that the formula, being symmetrical is in harmony with the well-established fact of the identity of the products irrespective of the order of combination:—

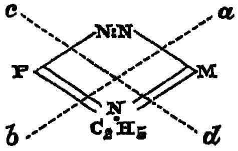


Then, again, the formation of *mixed products* on decomposition by hydrochloric acid is also accounted for. Giving the letters P and M the same meaning as before:—





If separation took place along *ab*, the products (with cold acid) would be paranitrodiazobenzene-chloride and metanitraniline; along *cd* the products would be metanitrodiazobenzene-chloride and paranitraniline. Since all four products are formed, it must be supposed that decomposition takes place along both lines, or, in other words, that the substance is decomposed along *ab* and *cd* in about equal quantities. The same explanation obviously applies to the ethyl-derivative :—



If the above formula be assigned to the ethyl-derivative (m. p. 148°) there then remains Kekulé's formula, or some modification thereof, for the other two ethyl-derivatives, and the remaining difficulty, the existence of three isomeric ethyl-derivatives, may perhaps be thus disposed of. It must be pointed out, in conclusion, that the new formula does not necessarily exclude the possibility of compounds of Kekulé's type being formed as the first products when diazotised amines act on dissimilar amines, but the facts now made known certainly indicate that the final products cannot be formulated on that type.

ANNUAL GENERAL MEETING,

March 30th, 1887.

Dr. Hugo Müller, F.R.S., President, in the Chair.

In accordance with our bye-laws, I have the honour of bringing before you the Annual Report of the state of the Society.

I rejoice in being able once more to announce to you that the affairs of the Chemical Society are in a satisfactory state, and that the prosperous conditions which I had the good fortune to report to you on the last Anniversary have been maintained.

Beginning with the statistics of membership, the following table will serve to show at a glance how we stand in this respect.

Number of Fellows (Anniversary), March, 1886		1428
Since elected and paid admission fees		110
		1538
Removed on account of arrears	28	
Withdrawn	20	
Deceased	13	
		61
		1477
Increase	37	
Number of Honorary Members	31	
Deceased	1	
Present number of Honorary Fellows	30	30
Total number		1507

It will be seen that the number of our Members has increased to 1507, although we have to record an unusually large number of removals on account of arrears, and also a larger number who have withdrawn, whilst, on the other hand, the loss by death is somewhat less than last year.

The names of those who have been removed on account of arrears are the following: F. H. T. Allan; P. S. Brown; Robert Blair; Henry Child; G. Crampton; John Dale; Dr. Arthur Gamgee;

A. M. Graham; G. Jarmain; R. H. Jude; F. Jordan; Wm Marriott; J. E. Mayall; J. D. Mucklow; Dr. R. S. Marsden; John McCarthy; A. A. Nesbit; F. J. O'Farrell; Alfred Payne; A. W. Postans; J. E. H. Richardson; F. I. Seard; J. Steiner; K. Takemura; G. Valentine; Stephen Williams; and James Wilson.

The names of those who have withdrawn are: W. E. Benton; T. F. Best; L. M. Deane; A. F. Dimmock; H. W. Field; W. J. Fuller; A. E. Garrod; Norman Graham; Thos. Harrison; Thos. Jamieson; Herbert Jones; Paul Mathews; P. B. Mills; J. D. McCarthy; Dr. A. P. Page; Dr. Robert Smith; G. Tunbridge; James Steel; A. H. Scott White; Philip Wright; and Wm. Cort Wright.

The names of the deceased Members are: one Honorary Member, Prof. A. Butlerow; Robert Alexander; Dr. James Apjohn, F.R.S.; Prof. F. S. Barff; Richard Cowper; M. G. Crossman; H. Sugden Evans; Rev. W. Flett; George Hirst; Dr. A. P. Price; J. A. Phillips, F.R.S.; F. Sear; E. R. Southby; and H. H. Watson.

The obituary notices of the deceased Members, as far as we have been able to obtain them, will be given in a later part of the Report.

There is nothing to record with respect to our publications, except that our Editors have discharged their duties in a most efficient manner, both in regard to the editorial work, and as to the regularity in the issue of the monthly numbers of the Journal.

The Society is much indebted to the Honorary Secretaries for the zeal with which they continue to edit the "Abstracts of Proceedings," which form so valuable an adjunct to our Journal.

It may be of some interest to bring before you the following table, which shows the number of Abstracts and papers in the Transactions published in our Journal during the last five years:—

	1882.	1883.	1884.	1885.	1886.
General and Physical Chemistry..	219	205	237	331	235
Inorganic Chemistry............	188	189	180	191	223
Mineralogical Chemistry	135	204	192	201	223
Organic Chemistry	837	739	939	1017	1056
Physiological Chemistry	112	73	118	142	100
Chemistry of Vegetable Physiology and Agriculture	270	163	324	218	160
Analytical Chemistry	284	195	256	337	289
Technical Chemistry............	228	212	286	280	66*
Total	2273	1980	2541	2747	2352
Papers in Transactions..........	65.	63.	57.	85.	85.

* The Technical Division was discontinued after the April Number, 1886.

Since January, 1886, an alphabetical index of Author's names has been given in each number.

In connection with the Library, I have only to mention that during the temporary absence of Dr. Thorne, Mr. Greenaway has undertaken his duties as Librarian. The card-catalogue of Author's names is now completed, and the catalogue of subjects has been revised up to letter S. During the last year, we availed ourselves of an opportunity of purchasing a considerable number of books on Alchemy and other works of historical interest, which form an important addition to the library.

I have to state with regard to the Research Fund that during the past year seven applications have been granted by the Research Fund Committee, amounting altogether to £170. This item somewhat exceeds the corresponding one of last year, although the number of applications is less.

Notwithstanding the fact that the number of Members actually elected during the last session is about the same as in the previous year, the present financial aspect of our Society is perhaps not quite so favourable, but as your Treasurer will presently give in his detailed account a full explanation as to how this is brought about, I need not here enter more fully upon it.

In proceeding to the consideration of what must ever remain our principal aim, it is especially gratifying to refer to the very noteworthy increase in the number of communications presented to the Society.

The following is a list of the papers read at the meetings during the past year, given in the order in which they have been received:—

Papers contributed to the Chemical Society between March 30th, 1886, *and March 30th,* 1887.

April 1st.

I. "The Determination of Boiling Points:" by W. Ramsay, Ph.D., and Sydney Young, D.Sc.

II. "The Vapour-pressures of Bromine and Iodine, and Iodine Monochloride:" by W. Ramsay and Sydney Young, Ph.D., D.Sc.

III. "The Use of the Electric Light to Influence Chemical Change:" by Henry E. Armstrong, Ph.D.

IV. "Some Sulphur Compounds of Barium:" by V. H. Veley, M.A.

V. "Parabenzylphenol and its Derivatives, and a New Benzylphenol:" by E. H. Rennie, M.A., D.Sc.

VI. "Amidodiphenylsulphonic Acid and Azo-dyes from Diphenyl:" by T. Carnelley, D.Sc., and James Schlosselman

April 15th.

VII. "The Eurhodines, a New Class of Colouring Matters:" by Otto N. Witt, Ph.D.

VIII. "The Action of Sodium on Ethereal Salts of Phenylacetic Acid. Part II:" by W. R. Hodgkinson, Ph.D.

IX. "The Action of Metals on Acids:" by Henry E. Armstrong, Ph.D.

May 6th.

X. "Paranitrobenzoylacetic Acid and some of its Derivatives:" by W. H. Perkin, Jun., Ph.D., and E. Bellenot, Ph.D.

XI. "An Acetic Ferment which forms Cellulose:" by Adrian J. Brown.

May 20th.

XII. "Sources of Error in the Calorimetric Study of Salts:" by W. A. Tilden, D.Sc.

XIII "On the Action of Aldehydes and Ammonia on Benzil:" by F. R. Japp, M.A., Ph.D., and W. Palmer Wynne, B.Sc.

XIV. "On Imabenzil:" by the same.

XV. "On Ammonia-derivatives of Benzoïn:" by Francis R. Japp, M.A., Ph.D., and W. H. Wilson, Ph.D.

XVI. "On Compounds from Benzil and Benzoin and Alcohols:" by Francis R. Japp, M.A., Ph.D., and Julius Raschen.

XVII. "On the Action of Phosphoric Sulphide on Benzophenone:" by the same.

XVIII. "The Separation and Estimation of Zirconium by means of Hydrogen Peroxide:" by G. H. Bailey, D.Sc.

XIX. "An Apparatus for the Determination of the Temperature of Decomposition of Salts:" by G. H. Bailey, D.Sc.

XX. "The Retention of Lead Salts by Filter-paper:" by L. Trant O'Shea.

June 3rd.

XXI. "Notes on Sir W. Fairbairn's Experiments on Remelting Cast Iron:" by Thomas Turner, Assoc. R.S.M.

XXII. "Some Ammonium Compounds and other Derivatives of α-1′ Hydroxyquinoline:" by C. H. Kohn, B.Sc., Ph.D.

XXIII. "β-Sulphophthalic Acid:" by C. Graebe, Ph.D., and A. Rée, Ph.D.

XXIV. "Compounds obtained by the aid of β-Sulphophthalic Acid:" by the same.

XXV. "Derivatives of Taurine." Part II: by J. William James, Ph.D.

June 17th.

XXVI. "The Electrolysis of Aqueous Solutions of Sulphuric Acid, with Special Reference to the Forms of Oxygen obtained:" by H. McLeod, F.R.S.

XXVII. "Essential Oils (Part III): their Specific Refractive and Dispersive Power:" by J. H. Gladstone, Ph.D.

XXVIII. "The Formation and Destruction of Nitrates and Nitrites in Artificial Solutions and in River and Well Waters:" by J. M. H. Munro, D.Sc.

XXIX. "Water of Crystallisation:" by W. W. J. Nicol, M.A., D.Sc.

XXX. "A Method of Investigating the Constitution of Azo-, Diazo-, and Analogous Compounds:" by R. Meldola, F.R.S., and F. W. Streatfeild.

XXXI. "The Estimation of Free Oxygen in Water:" by Miss K. I. Williams and W. Ramsay, Ph.D.

XXXII. "Note as to the Existence of an Allotropic Modification of Nitrogen:" by Miss K. I. Williams and W. Ramsay, Ph.D.

XXXIII. "The Presence of a Reducing Agent, probably Hydrogen Peroxide, in Natural Water:" by W. Ramsay, Ph.D.

XXXIV. "Evaporation and Dissociation. Part IV. A Study of the Thermal Properties of Acetic Acid:" by W. Ramsay, Ph.D., and Sydney Young, D.Sc.

XXXV. "Note on the Vapour-densities of Chloral Ethyl-Alcoholate:" by the same.

XXXVI. "The Nature of Liquids as shown by a Study of the Thermal Properties of Stable and of Dissociable Bodies:" by the same.

XXXVII. "The Electromotive Forces developed during the Combination of Cadmium and Iodine in Presence of Water:" by A. P. Laurie, B.A., B.Sc.

XXXVIII. "Detection and Estimation of Iodine, Bromine, and Chlorine:" by M. Dechan.

XXXIX. "The Analysis of Alloys and Minerals containing the Heavy Metals, Selenium, Tellurium, &c.:" by Thomas Bayley.

apers Contributed to the Society during the Months of July, August, September and October.

XL. "Phenylsulphonic Anhydride:" by J. L. H. Abrahall.

XLI. "The Action of Hexabromacetone on Urea:" by Alfred Senier, M.D.

XLII. "Contributions to our Knowledge of the Chlorides of Antimony:" by Richard Anschutz and P. Norman Evans.

XLIII. "Pipitzahoic Acid." (First Communication): by Richard Anschutz and John Walter Leather.

XLIV. "Further Contributions to the Knowledge of Cyanuric Chloride and other Cyanuric Derivatives:" by Harold H. Fries.

XLV. "Further Observations on the Action of Hexabromacetone on Urea:" by Alfred Senier.

XLVI. "The Constitution of Diazobenzeneanilide and its Relation to Amidoazobenzene." II: by R. J. Friswell and A. G. Green.

XLVII. "Determinations of Vapour-pressures of Alcohols and Organic Acids, and the Relations existing between the Vapour-pressures of the Alcohols and Organic Acids:" by Arthur Richardson, Ph.D.

XLVIII. "The Magnetic Rotation of Mixtures of Water with some of the Acids of the Fatty Series, with Alcohol and with Sulphuric Acid; and Observations on Water of Crystallisation:" by W. H. Perkin, Ph.D., F.R.S.

XLIX. "Trimethyldiethylamidobenzene:" by R. F. Ruttan, B.A., M.D.

L. "The Action of Bromine on Phosphorus Trichloride:" by A. L. Stern.

LI. "The Electrolytic Preparation of Vanadious Sulphate:" by J. T. Brierley.

November 4th.

LII. "The Action of Chlorosulphonic Acid on Naphthalene-α- and β-Sulphonic Acids:" by Henry E. Armstrong, Ph.D., and W. P. Wynne, B.Sc.

LIII. "The Action of Bromine on (Schaefer's) β-Naphtholsulphonic Acid:" by Henry E. Armstrong, Ph.D., and F. W. Streatfeild.

LIV. "The Action of Bromine on the Naphthalenesulphonic Acids:" by Henry E. Armstrong, Ph.D., and W. P. Wynne, B.Sc.

LV. "α-Nitro-, α-Bromo-, and α-Chloronaphthalenesulphonic Acids:" by Henry E. Armstrong, Ph.D., and S. Williamson.

LVI. "The Hydrolysis of Sulphonic Acids:" by A. K. Miller, Ph.D.

LVII. "The Action of Bromine on Tolueneparasulphonic Acid:" by the same.

LVIII. "Phosphorus Tetroxide:" by T. E. Thorpe, Ph.D., and A. E. Tutton.

LIX. "Conversion of Ditolane-azotide into Diphenanthrylene-azotide:" by Francis R. Japp, M.A., Ph.D., and Cosmo Innes Burton, B.Sc.

LX. "A Chemical Study of Vegetable Albinism. Part III. Experiments with *Quercus rubra:*" by A. H. Church.

LXI. "The Synthetical Formation of Closed Carbon-chains. Part II. Some Derivatives of Tetramethylene:" by W. H. Perkin, Jun., Ph.D.

LXII. "The Action of the Halogens on the Salts of Organic Bases. Part II. Tetramethylammonium Salts:" by Leonard Dobbin, Ph.D., and Orme Masson, M.A., D.Sc.

LXIII. "Glycyphyllin, the Sweet Principle of *Smilax glycyphylla:*" by Edward H. Rennie, M.A., D.Sc.

November 18th.

LXIV. "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra. Part VIII. A Study of Coloured Substances and Dyes:" by W. N. Hartley, F R.S.

LXV. "Spectroscopic Notes on the Carbohydrates and Albuminoids from Grain:" by W. N. Hartley, F.R.S.

LXVI. "Preliminary Note on the Electrolysis of Ammonic Sulphate:" by Herbert McLeod, F.R.S.

LXVII. "The Preparation and Hydrolysis of Hydrocyanides of the Diketones:" by Francis R. Japp, M.A., Ph.D., and N. H. J. Miller, Ph.D.

LXVIII. "The Action of Salicylic Aldehyde on Sodium Succinate in presence of Acetic Anhydride:" by Gibson Dyson, Ph.D.

LXIX. "The Reduction of Nitrites to Hydroxylamine by Hydrogen Sulphide:" by E. Divers, F.R.S., and T. Haga.

LXX. "Note on some Double Thiosulphates:" by J. B. Cohen, Ph.D.

LXXI. "Preliminary Note on the Action of Triphenylmethyl

Bromide on Ethyl Sodio-malonate:" by George G. Henderson, M.A., B.Sc.

LXXII. "Action of Silicon Tetrachloride on Aromatic Amido-compounds:" by Arthur Harden, B.Sc.

December 2nd.

LXXIII. "Bismuthates:" by M. M. Pattison Muir and Douglas J. Carnegie.

LXXIV. "The Action of Inorganic Compounds on Living Matter:" by James Blake, M.D.

LXXV. "Morindin and Morindon:" by T. E. Thorpe, Ph.D., and T. H. Greenall.

LXXVI. "The Hydration of Salts: Cadmium Chloride:" by S. U. Pickering, M.A.

LXXVII. "The Decomposition of Sodium Carbonate on Fusion:" by S. U. Pickering, M.A.

LXXVIII. "Derivatives of Tolylbenzene:" by Thomas Carnelley, D Sc, and Andrew Thomson, D Sc.

LXXIX. "The Amount of Chlorine in Rain-water collected at Cirencester:" by Edward Kinch.

LXXX. "Some Analogous Phosphates, Arsenates, and Vanadates:" by John A. Hall.

LXXXI. "Agricultural Experiments with Iron Sulphate as a Manure during 1886:" by A. B. Griffiths, Ph.D.

December 16th.

LXXXII. "Researches on the Constitution of 'Azo- and Diazo-derivatives.' I. Diazoamido-compounds:" by R. Meldola, F.R.S., and F. W. Streatfeild.

LXXXIII. "The Influence of Silicon on the Properties of Iron and Steel:" Part I: by Thomas Turner, Assoc. R.S.M.

LXXXIV. "The Distribution of Nitrifying Organisms in the Soil:" by R. Warington, F.R.S.

LXXXV. "Isomeric Change in the Phenol Series. The Action of Bromine on the Dibromonitrophenols:" by A. R. Ling.

LXXXVI. "Some Azines:" by Francis R. Japp, M.A., Ph.D., and Cosmo Innes Burton, B.Sc.

January 20th, 1887.

LXXXVII. "Some Silicon Compounds and their Derivatives:" by J. Emerson Reynolds, M.D.

LXXXVIII. "Chrom-organic Acids. Part I. Certain Chrom-oxalates:" by Emil A. Werner.

LXXXIX. "Note on the Constitution of the Double Chromic Oxalates:" by W. N. Hartley, F.R.S.

XC. "Remarks on recent Papers by A. Baeyer and J. Thomson, on 'The Constitution of Benzene:'" by A. K. Miller, Ph.D.

February 3rd.

XCI. "The Absorption of Gases by Carbon:" by Charles J. Baker.

XCII. "An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds:" by Henry E. Armstrong, Ph D.

XCIII. "Some Derivatives of Tetramethylene:" by G. H. Colman, B Sc., and Dr. W. H. Perkin, Jun., Ph.D.

XCIV. "Derivatives of Pentamethylene:" by Dr. W. H. Perkin, Jun., Ph.D.

XCV. "The Decomposition of Potassium Chlorate and Perchlorate by Heat:" by Percy F. Frankland, Ph.D., B.Sc., and John Dingwall.

XCVI. "The Action of Chlorine on Methyl Thiocyanate:" by J. William James, Ph.D.

February 17th.

XCVII. "The Influence of Temperature on the Heat of Dissolution of Salts;" by S U. Pickering, M A.

XCVIII. "Periodates:" by C. W. Kimmins, D.Sc., B.A.

XCIX. "Sulphonic Acids derived from the β-Monohaloid-derivatives of Naphthalene:" by Henry E. Armstrong, Ph.D., and W. P. Wynne, B.Sc.

C. "The Decomposition of Potassium Chlorate and Perchlorate by Heat:" by Frank L. Teed, D.Sc.

CI. "The Formation of Ethylic Cyanacetoacetate:" by J. William James, Ph.D.

CII. "The Relation of Diazobenzene-anilide to Amidoazobenzene:" by R. J. Friswell and A. G. Green.

CIII. "Note on Wallach's Explanation of the Isomeric Transformation of Diazoamidobenzene into Amidoazobenzene:" by R. Meldola, F.R.S.

March 3rd.

CIV. "Tartaric and Racemic Acids and the Magnetic Rotatory

Power of their Ethyl Salts:" by W. H. Perkin, Ph.D., F.R.S.

CV. "Anhydracetonebenzil:" by Francis R. Japp, M.A., Ph.D., and Cosmo Innes Burton, B.Sc.

CVI. "Condensation Compounds of Benzil with Ketones:" by the same.

CVII. "Constitution of Glycosine:" by Francis R. Japp, M.A., Ph.D., and E. Cleminshaw, M.A.

CVIII. "Diphenylglyoxaline and Methyldiphenylglyoxaline:" by Francis R. Japp, M.A., Ph.D.

CIX. "Dehydracetic Acid:" by W. H. Perkin, Jun., Ph.D.

CX. "The Colouring Matter of *Drosera Whittakeri*:" by Professor E. H. Rennie, M.A., D.Sc.

CXI. "Further Notes on the Di-haloid Derivatives of Thiocarbamide:" by George McGowan, Ph.D.

March 17th.

CXII. "The Action of Heat on Nitrogen Peroxide:" by A. Richardson, Ph.D.

CXIII. "Supersaturation of Salt Solutions:" by W. W. J. Nicol, M.A., D.Sc.

CXV. "The Formation of γ-Naphthalenesulphonic Acid by means of Sulphuric Anhydride, and on γ-Dihydroxynaphthalene:" by Henry E. Armstrong, Ph.D., and W. P. Wynne, B.Sc.

CXIV. "α-Cyanonaphthalenesulphonic Acid:" by Henry E. Armstrong, Ph.D., and S. Williamson.

CXVI. "Addendum to Paper entitled 'An Explanation of the Laws which govern Substitution in the case of Benzenoid Compounds:' by Henry E. Armstrong, Ph.D.

CXVII. "The Transformation of Citric Acid into Pyridine-derivatives, and on the Constitution of Pyridine:" by S. Ruhemann, Ph.D.

CXVIII. "Silver containing Bismuth:" by William Gowland, A.R.S.M.

Comparing these numbers with those of last year, we have an increase of 14, which again exceeds by 5 the largest number communicated in any previous session, namely, that of 113, which was reached in 1880–81.

In reviewing this list, it seems to me that we have great reason to be satisfied with the share this Society has contributed towards the general progress of our science in its various branches, and the anticipation which I expressed at the last Anniversary that this marked expansion then noted in the direction of scientific chemical research may be a lasting one has thus far been fully realised.

As we contemplate this ceaseless activity in chemical research now manifested all over the world, and which from year to year is continually on the increase, we are nevertheless bound to recognise the fact that vast as the work thus accumulated may appear, there remains still much to be accomplished. The more the field is worked the richer will be the harvest.

Overwhelmed by the quantity of material, especially in the direction of the production of new compounds, hasty critics were wont to denounce such work as superfluous, but it is now generally recognised that we must still continue with the patient and careful elaboration of the substructure of facts before we can with advantage proceed with the longed-for rearing of the edifice of a comprehensive scientific generalisation, that is to say of ideal chemistry.

The infinite complexity which inquiry reveals in every direction bids us more than ever to be cautious in taking flight on the wings of speculation, and in the meantime we must content ourselves with the use of working hypotheses in the various fields of enquiry; these we develop and modify as we go on, or it may be discard in favour of others which for the time being seem more in accordance with the facts before us.

The triumphs of modern chemistry bear testimony that faulty and incomplete as our present theories undoubtedly are, our science is ever advancing.

It is now well understood that the most important data for the future extension of chemical theory will be derived from the interpretation of the results of investigations into the physical side of chemical phenomena.

The examination of the optical properties of chemical elements and compounds, the determination of thermochemical constants, and the verification of physical constants generally, are now pursued by a great number of investigators. Of late also the experimental enquiry into the connection between electrical and chemical force is becoming a fruitful field of research; and we may hope that further determinations of the coefficients of conductivity of electrolytes will before long lead to a clearer perception of the intimate nature of chemical change.

To pass in review the chemical work published during the year, as some of my predecessors have done on similar occasions, has now become an impossible task, even supposing that the time at my disposal permitted me to do so. I am, however, tempted to refer briefly to a few results which strike me as particularly noteworthy.

The work accomplished in thermochemistry is very considerable, as I have already observed, and thanks to the patient labour of many workers the results thus achieved are comprehensive enough to admit of a consideration of their general bearings. In this respect I wish to direct attention to the publication of Julius Thomsen's fourth and concluding volume of "Thermo-chemische Untersuchungen." This remarkable work is entitled to the highest appreciation of all who realise the manifold difficulties which beset the execution of thermochemical investigation. But while referring to the many highly important and remarkable deductions which the author draws from his experiments, we cannot at the same time help being struck by the many anomalous results and startling conclusions at which he arrives. It would seem that further determinations of the fundamental values, if possible by different and varied experimental methods, must be obtained before the full importance of this work can be entirely realised.

An important addition to our still very limited knowledge of the density of metallic elements in the gaseous state has been made by V. Meyer and Mensching, who have now succeeded in overcoming the great experimental difficulties formerly encountered in the determination of the vapour-density of zinc. The molecule of zinc has been found to be monatomic, like that of cadmium and of mercury, the only two other metals the vapour-densities of which are thus far known.

The remarkable results recently published by Crookes in his papers on the spectra of the so-called rare earths are still fresh in our memory, and the ingenious application he has made of the doctrine of evolution in this speculation on the genesis of the elements has not failed to attract the attention it deserves.

The further investigations of the chemical and physical properties of the new element germanium by Winkler, Nilson and Pettersson have established its chemical position, and the supposition that its proper place in the periodic system is that of ekasilicon has been confirmed.

Ladenburg's long-continued researches on conine have been crowned by success. He has effected its synthesis and has shown that it is identical with α-propylpiperidine. This must indeed be considered one of the most noteworthy achievements in organic chemistry of the past year, inasmuch as it is the first instance of the artificial formation of an optically active natural alkaloïd.

Wallach found that the diazo-amido-compounds formed from diazo-salts and piperidine are for the most part well-characterised substances, and that when heated with concentrated hydrofluoric acid they yield the fluor-derivative in almost theoretical proportions. He has prepared in this way fluorbenzene, parafluortoluene, parafluornitrobenzene, parafluoraniline, and fluorphenyl, &c.

Studying the action of sodium on mixtures of ethers such as oxalic and acetic ethers, W. Wislicenus has discovered a new and ready method of effecting the synthesis of compound acids, and this reaction cannot fail to become of great value.

Brieger has succeeded in isolating a well-characterised alkaloïd from the liquid used for cultivating a certain bacillus which causes traumatic tetanus in animals. This substance, which the author calls tetanine, seems to be the immediate cause of the toxic action of this bacillus, and thus for the first time a specific pathological effect of a microbe has been traced to a well-defined chemical compound produced or secreted in its life-process.

Finally, I must also allude to the very remarkable observation recently published by Liebreich, which demonstrates the fact that under certain conditions chemical reaction is retarded and even altogether suspended. He noticed that in a mixture of aqueous solutions of chloral hydrate and sodium carbonate the formation of chloroform does not take place uniformly throughout the liquid. For instance, on performing the experiment in a test-tube there appears immediately below the meniscus a sharply defined space of 1—3 mm. thickness in which no reaction takes place. Similar results were obtained when an aqueous solution of iodic acid was mixed with sulphurous acid and soluble starch. The inert space manifests itself on the surface of the liquid which is in contact with the air, or is separated from it by a thin membrane. In narrow tubes the reaction is much more retarded, and it is altogether suspended in capillary tubes.

In my opinion this preliminary communication contains the germs of a discovery in a new direction, and the further study of the nature of the subtle influences which bring about the phenomenon in question, must lead to very important results.

In bringing this Report to a conclusion, I must briefly allude to a subject only indirectly connected with our Society, viz., the progress made in the organisation of technical education in this country, which more particularly under the guidance and fostering care of the City and Guilds of London Institute is gradually making its way.

Most of you are aware that the President of this Society is one of the *ex-officio* members of the governing and organising body of this Institute, and it may be mentioned in passing that the regular attendance at the frequent meetings of the various Committees and Sub-Committees involves the necessity of devoting a by no means inconsiderable amount of time to this honorary office.

The chief event to be recorded in this connection is the inauguration of the Central Institution which is to fulfil the function of a Technical University or Polytechnicum, and to afford higher scientific education to the future owners, directors, managers, engineers of manufacturing works, and the teachers in the various branches of technology. This magnificent Institution has now started on its career, and we have every reason to think that before long its value will be fully recognised by those who ought to take advantage of its existence. It is, however, unfortunate that the organisation of this Institution has stopped short of the plans originally laid down, and has been not at once carried to completion. Strange as it may appear this is due to the want of funds. The City and Guilds in taking so prominently charge of the initiation and diffusion of technical education in this country, have thus far most liberally furnished the means required, and have thus earned the gratitude of the country, but as the development of the scheme progresses an even and commensurate flow of further contributions is required which, being voted in many cases but annually, at once demonstrates the somewhat precarious conditions on which this important enterprise is dependent.

It is to be hoped that a more general recognition of the absolute need of an education of a higher scientific character for masters as for men will before long have its proper effect in bringing forth the ways and means necessary to carry out and develope a work which promises so well. The Central Institution may then stand a fair comparison with numerous institutions of a similar kind in other countries which have already helped in so marked a degree to advance the industries of those countries.

The mistaken notion is still too prevalent that technical education has to confine itself to the theoretical considerations of known technical processes, and that a more extended acquisition of scientific knowledge is not required or is even not desirable. It is obvious that a pupil educated on these lines may find by the time he is able to enter on his practical career that the processes with which he has been made acquainted have in the meanwhile become obsolete, and unless his education has been sufficiently comprehensive to enable him to strike out new lines for himself, he will be ill fitted to compete with those who have been educated on a wider basis.

Essential as it is to impart scientific knowledge to the future manager, it is above all necessary to train him by practical work and research in the laboratory how to investigate a subject which may present itself in his daily occupation, whether it be some unexpected development in a new direction, or whether it be some new difficulty which confronts him in carrying out the processes under his direction.

It is self-evident that such knowledge and such practical experience in carrying out original research or investigations is not to be attained by merely attending one or two courses in the lecture room or in the laboratory. Those who mean to effectually qualify themselves for such functions can only accomplish this object by devoting years of patient and intelligent work under the guidance of the professor in properly appointed laboratories.

Prof. Odling proposed that the thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. This motion was seconded by Dr. Gladstone, and accepted with acclamation by the Fellows present; the President acknowledged the compliment.

Professor Ramsay moved that thanks for their important services be given to the Editor, Sub-editor, Abstractors, and Librarian; the motion was supported by Mr. Dunstan. Mr. Groves replied.

Dr. A. K. Miller and Dr. Rideal were then appointed scrutators, and a ballot having been taken, the following were declared elected as Officers and Council for the ensuing year:—

President: W. Crookes, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; Warren de la Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S,

Vice-Presidents: J. Dewar, M.A., F.R.S.; David Howard; H. McLeod, F.R.S.; Ludwig Mond; C. Schorlemmer, Ph.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, M.A., Ph.D., F.R.S.

Treasurer: W. J. Russell, Ph.D., F.R.S.

Ordinary Members of Council: Messrs. T. Carnelley, D.Sc.; M. Carteighe; A. H. Church; Frank Clowes, D.Sc.; P. F. Frankland, Ph.D.; R. J. Friswell; E. Kinch; R. Messel, Ph.D.; H. F. Morley, M.A.; J. A. R. Newlands; W. Ramsay, Ph.D.; Thomas Stevenson, M.D.

The Treasurer, Dr. Russell, gave an account of the Society's financial condition. The receipts by admission fees and subscriptions had been £2999 2*s.*; by sale of Journal, £369 19*s.* 2*d.*; by dividends on invested capital, £305 0*s.* 9*d.* The expenses on account of the Journal had been £2026 16*s.* 9*d.*; on account of the Abstracts of

	£	s.	d.	£	s.	d.
Balance at Bank March 22nd, 1886	1,529	12	10			
" in hands of Treasurer	0	8	8			
				1,530	1	6
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 22nd, 1886, to March 21st, 1887.						
17 Life Compositions	340	0	0			
113 Admission Fees	452	0	0			
1 Subscription for 1883	2	0	0			
17 " " 1884	34	0	0			
77 " " 1885	154	0	0			
313 " " 1886	619	0	0			
717 " " 1887	1,398	2	0			
				2,999	2	0
Sale of Journal and Index				365	19	2
Subscriptions for Proceedings of Royal Society				46	0	0
" from Institute of Chemistry				7	0	0
" from Society of Public Analysts				4	4	0
Dividend on Consols				116	0	0
" Metropolitan Board of Works 3½ per Cent. Stock				158	3	5
" London and North Western Railway Debenture Stock				30	9	4
				5,256	19	5

Assets.	£	s.	d.
Balance at Bank	1,297	3	0
" in hands of Treasurer	4	7	3
Three per Cent. Consols	4,000	0	0
London and North Western Railway Debenture Stock	788	0	0
Metropolitan Board of Works 3½ per cent. Stock	4,800	0	0

	£	s.	d.	£	s.	d.
Expenses on Account of the Journal.						
Salary of the Editor	250	0	0			
Salary of the Sub-Editor	100	0	0			
Incidental Expenses of Editor	2	14	7			
Fees to Abstractors	241	11	5			
Printing of Journal	1,178	6	1			
Distribution of Journal	247	0	8			
Periodicals for Abstractors	7	4	0			
				2,026	16	9
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
" Library Attendant	62	0	0			
Books and Periodicals	170	14	2			
Binding	40	17	8			
				323	11	10
Printing Authors' Copies				44	10	0
Proceedings of Royal Society (2 years)				120	0	0
Distributing Proceedings of Royal Society				3	15	9
Printing and Distributing Abstracts of Proceedings				163	4	11
Post Cards of Lists of Meetings				2	1	6
Printing, Binding, and Distributing Catalogue				249	0	0
Miscellaneous Printing				62	13	2
Inhabited House Duty and Income-tax				10	8	9
Stationery and Receipt Books				42	18	4
Furniture and Repairs				33	14	9
Collector's Commission on Subscriptions				149	19	0
Treasurer's Stamps and Drafts				4	12	7
House Expenses.						
Providing Refreshments	20	4	9			
Heating the Building	18	14	0			
Lighting "	50	19	3			
Cleaning "	20	0	0			
House Expenses	10	7	5			
Wages of House Porter	53	0	0			
				173	5	5
Treasurer's Petty Cash Disbursements				6	1	5
Purchase of £500 Metropolitan Board of Works 3½ per cent. Stock				538	15	0
Balance at Bank	1,297	3	0			
" in hands of Treasurer	4	7	3			
				1,301	10	3
				5,256	19	5

Audited and found correct with vouchers.
WYNDHAM R. DUNSTAN.
C. W. HEATON.
PERCY F. FRANKLAND.

March 24th, 1887.

Treasurer of the Chemical Society in Account with Research Fund.

From March 22nd, 1886, till March 21st, 1887.

Dr.		£	s.	d.	Cr.	£	s.	d.
1886.					1887.			
Mar. 22.	Balance at Bank	343	3	8	Grants made	145	0	0
Aug. 17.	Subscription from Drapers' Company	105	0	0	Purchase of £200 Stock in Metropolitan Board of Works 3½ per cent. Stock	215	10	0
	Dividends on Metropolitan Board of Works Stock................................	130	5	2	Balance at Bank	237	5	6
	Dividend on North British Railway Stock ..	19	6	8				
		£597	15	6		£597	15	6

Assets.	£	s.	d.
North British Railway 4 per cent. Stock ..	1,000	0	0
Metropolitan Board of Works 3½ per cent Stock	3,900	0	0
Balance at Bank	237	5	6

Audited and found to be correct
with vouchers,
March 24th, 1887.

Wyndham R. Dunstan.
C. W Heaton.
Percy F. Frankland.

Proceedings, £163 4*s.* 11*d.*; on account of the Library, £323 11*s.* 10*d.*; on account of the Catalogue, £249; the total expenses being £3416 14*s.* 2*d.*; £500 had been invested in Metropolitan Board of Works 3½ per cent. stock, and there was a balance in hand of £1301 10*s.* 3*d.*

Mr. David Howard moved that the thanks of the Society be tendered to the Treasurer for his services during the past year; Mr. Friswell seconded the motion. The Treasurer in the course of his reply took occasion to point out that the expenses connected with the issue of the circular relating to the Imperial Institute and the collection of contributions thereto would not be borne by the Society, and that his connexion with the fund was a purely private one.

Mr. J. Spiller proposed a vote of thanks to the Auditors, which was seconded by Dr. H. F. Morley, and acknowledged by Mr. Wyndham Dunstan.

A vote of thanks to the Officers, Council, and Committee, was proposed by Mr. Warington, seconded by Mr. Davies, and acknowledged by Dr. Armstrong.

OBITUARY NOTICES.

JAMES APJOHN was born at Sunville, Co. Limerick, on the 1st of September, 1796, and, having received his elementary education at the Tipperary Grammar School, he entered Dublin University in 1814. After a distinguished undergraduate course, he took his Arts degree in 1817, and in 1821 the degree of M.B., and 16 years later he proceeded to the M.D degree. Apjohn's love for experimental science seems to have developed during his medical studies, and after graduating he devoted himself almost exclusively to the pursuit of chemistry and physics. About 1824 several eminent physicians and surgeons—including Groves, Marsh, Jacob, and Cusack—decided to establish a new medical school at Parke Street, in Dublin, and in the following year Apjohn joined the staff of the new school as Lecturer in Chemistry. Here he acquired considerable reputation as a lecturer, and three years later he was transferred to the newly-established Chair of Chemistry in the College of Surgeons' School, which he held until 1850, when he was appointed to the University Chair of Chemistry on the death of Dr. Francis Barker. Apjohn's official connection with the University began, however, in 1841; about that time the Board of Trinity College founded an Engineering School, and appointed Apjohn to the Chair of Applied Chemistry and Mineralogy—

an office which he continued to hold when he succeeded Barker in 1850. Dr. Apjohn retired from the Professorship of Chemistry in the University of Dublin in 1875. He died on the 2nd of June, 1886, at Southill, Blackrock, Co. Dublin, in his ninety-first year.

The principal scientific work of Dr. Apjohn was rather physical than chemical. The general study of hygrometry had a special attraction for him, and of the 49 scientific papers named in the Royal Society's Catalogue, a large proportion relates to that subject. In the course of his work on the theory of the wet bulb hygrometer, he arrived at the expression well known as "Apjohn's Formula" for ascertaining the dew point.

The study of hygrometry led to much interesting work on the specific heat of gases, and in 1837 Apjohn received the Cunningham Medal from the Irish Academy for his paper "Upon a New Method of Investigating the Specific Heats of the Gases." The method consisted in noting the fall in temperature suffered by the wet bulb thermometer when immersed in the perfectly dry gas whose specific heat was required. From 1838 Dr. Apjohn devoted less attention to physical work than to mineralogical chemistry. In 1838 he analysed and described a mineral from Algoa Bay, South Africa, which proved to be a somewhat effloresced manganese alum, which has since been named "Apjohnite." In 1840 he described a mineral from Kilbricken, Co. Clare, which is closely related to geocronite, but is non-arsenical. Again, in 1852 he was concerned in the description, under the name of "Jellettite," of a yellowish-green garnet found near Zermatt, by Dr. Jellett, the present Provost of Trinity College. Papers on the relations of pyrope, of pennine, and on Mexican hyalite are also to be found amongst his contributions to mineralogy.

Dr. Apjohn contributed to the "Cyclopædia of Practical Medicine" the articles on electricity, galvanism, toxicology, and spontaneous combustion, and as the representative of the University of Dublin in the General Medical Council, Dr. Apjohn took a prominent part in the production of the "British Pharmacopœia." Almost every chemical process and test described in the first edition of the "Pharmacopœia" was carefully examined in the Trinity College Laboratory, and much of the success of the work was due to Apjohn's laborious revision in detail.

He was elected a Fellow of the Royal Society in 1853, and a Fellow of the Chemical Society in 1861; he was a Vice-President of the Royal Irish Academy; and at the time of his death was second on the roll of Fellows of the King and Queen's College of Physicians.

Dr. Apjohn was widely esteemed throughout his long life as a thorough and earnest worker, a singularly lucid and able lecturer, and an upright and honourable man.

Frederick Settle Barff was the son of a doctor at Hackney, where he was born on October 6, 1823. Professor Barff was educated at Christ's College, Cambridge, and he took his degree of B.A. in 1844, proceeding to that of M.A. in the usual course. Shortly afterwards he was ordained a deacon in the Church of England, and began parochial work as curate of St. Nicholas, Leicester. He remained there about three years, when he became assistant-curate of Holy Trinity, Kingston-upon-Hull, a post which he resigned in 1852 on his reception into the Church of Rome. He remained a fervent and devout Roman Catholic to the day of his death. His interest in theology, both dogmatic and mystic, was always intense, and it was one of his favourite themes of conversation with his friends.

Thirty years ago there was not much opening for a clergyman who had renounced his orders, but fortunately Mr. Barff's mind was of a scientific bent, and he was soon drawn to study the manufacture of stained glass windows and church decoration generally. The best known result of his studies in these subjects at Munich is the part which he took in the painting of the frescoes at Stonyhurst. Afterwards he went to Dublin, whence he came to London in 1864, to study chemistry under Dr. Williamson at University College. He became Assistant Professor of Chemistry at University College, and retained that post until about 1870. In 1869 he published an "Introduction to Scientific Chemistry," which rapidly passed through several editions. In 1873 he brought out his "Elementary Chemistry," of which a second edition was demanded within two years.

Besides his contributions to scientific periodicals, Mr. Barff delivered before the Society of Arts, in 1870, a series of Cantor Lectures on "Artistic Colours and Pigments," and it was owing to the attention drawn to the subject of these lectures that the Chair of Chemistry was founded at the Royal Academy, and that Mr. Barff was appointed the first Professor. Professor Barff delivered a second course of Cantor Lectures, in 1872, on "Silicates, Silicides, Glass, and Glass Painting;" and another course, in 1874, on "Carbon, and Certain Compounds of Carbon, treated principally in reference to Heating and Illuminating Purposes." He also gave the Juvenile Lecture for 1878, on "Coal and its Compounds." For his paper on "Zinc White as Paint, and the Treatment of Iron for the Prevention of Corrosion," read in 1877, Mr. Barff received the Society's medal. In this paper he announced the discovery of his method of protecting iron from rust by producing a film of magnetic or black oxide of iron on the surface of the metal. In March, 1879, he read a second paper on his process for "The Treatment of Iron to Prevent Corrosion." In 1882, he obtained another medal for a paper on a "New Antiseptic Compound, and its Application to the Preservation of Food." Mr. Barff served as Examiner in Chemistry for the Natural Science Tripos at Cambridge, and held the office of Professor of Chemistry at the Roman Catholic University at Kensington, and in the Jesuits' College, Beaumont. He was elected a Fellow of the Chemical Society in 1867, and died at Buckingham, on the 11th August, in the sixty-third year of his age.

ALEXANDER MIKHAÏLOVITCH BUTLEROW was born on September 6th,* 1828, at Tchistopol, in the government of Kazan. His father was a Lieutenant-Colonel in the Imperial Army. At an early age he lost his parents, and was educated by his grandfather, Strelkoff. He attended the gymnasium in Kazan, and in 1844 entered the University of that town, where he turned his attention to physical science. He studied chemistry in Klaus' laboratory, the discoverer of ruthenium. Klaus was to the last a staunch adherent of the dualistic theory of Berzelius; but his influence in theoretical matters was, so far as Butlerow was concerned, modified by that of Nikolai Zinin, who held the chair of Technical Chemistry at Kazan until 1847, and by whose advice Butlerow later, in 1854, adopted Gerhardt's system in his lectures on chemistry.

Butlerow completed his studies in 1849, graduating as Candidate in Natural Science. In 1850, he commenced his lectures on chemistry, at the same time filling the post of assistant to Klaus in the chemical laboratory of the University. In 1851 he received the degree of Master of Chemistry, and was made Assistant Professor; in 1854 he obtained the Doctorate, with the rank of Extraordinary Professor; and in 1858 was promoted to the grade of Ordinary Professor. In 1857, and later in 1861, Butlerow visited the principal laboratories of Western Europe, making the acquaintance of a number of the leading chemists of the day. From 1860 to 1863, Butlerow was Rector of the University of Kazan. In 1868, he accepted a call to the chair of Chemistry in the University of St. Petersburg, and in 1870 was elected a Member of the Imperial Academy of Sciences. In St. Petersburg, he also delivered the lectures on chemistry in connection with the scheme for the higher education of women, from the inauguration of this scheme in 1877. He was elected a Foreign Member of the Chemical Society in 1876, and died on the 17th of August, 1886, having discharged his professional duties almost to the last.

Butlerow was an eloquent lecturer—one of the most eloquent lecturers among Russian professors of the past generation—and possessed, moreover, in a high degree the gifts of a successful laboratory teacher. These qualities, together with the interest which his original investigations inspired in his pupils, admirably fitted him to become, as he did, the founder and head of a school of chemists, many of whom now hold professional appointments in the various universities of Russia.

---

* New style.

The following is a list of Butlerow's most important investigations:—

His first published experimental work, dealing with the action of osmic acid on organic substances, appeared in 1852. It was followed by a series of short notes on various subjects. But it was not until 1858–59 that he began to take a prominent part in establishing the theory of structural formulæ. While working in Wurtz's laboratory. in Paris, he commenced an investigation of methylene iodide, which he afterwards continued in Kazan; and having studied various methylene-derivatives—the chloride, the bromide, trioxymethylene, and the product of the action of ammonia on trioxymethylene (hexamethylenetetramine)—he arrived at the conclusion that the radicle methylene is incapable of existing in the free state. He also synthesised from trioxymethylene a saccharoid substance—methylenitan—described by him in 1861.

The year 1862 saw Butlerow at work on a new subject—the synthesis of alcohols with the aid of organo-metallic compounds. It was by acting with zinc methyl on acetic chloride that he effected his important synthesis of trimethyl carbinol, the first known member of the series of the tertiary alcohols, the existence of which had been predicted by Kolbe. Whilst continuing the study of these alcohols, Butlerow published work dealing with other subjects; amongst these may be mentioned his determination of the vapour-density of lead methyl, from which he deduced the quadrivalence of lead. In 1872, he successfully attacked a new problem in the synthesis of trimethylacetic acid; and in 1875 he returned to the subject of the tertiary alcohols by preparing pentamethylethol (tertiary butyl dimethyl carbinol) from trimethacetic chloride and zinc methyl. In 1877, he published a research on di-isobutylene, and, in 1879 and 1882, on triisobutylene—products of the polymerisation of isobutylene with sulphuric acid. His last investigation, "On Asarone," the first part of which appeared in 1884, was completed just before his death, and was published about the beginning of the present year.

Butlerow's most important literary work was his "Introduction to the Study of Organic Chemistry," published in 1864; it was the first work of the kind in Russia in which structural formulæ were employed. It was translated into German in 1868, and, since the death of the author, has been re-edited by his pupils.

RICHARD COWPER, A.R.S.M., A.I.C., F.C.S, was born on December 3rd, 1855, at Kensington. His education was obtained partly at King's College School, where he remained from 1868 to 1871. He then went to the Royal School of Mines, where he took his Associateship in Mining and Metallurgy in 1874, having passed a specially brilliant examination in the latter subject. Mr. Cowper volunteered his assistance to the late Professor Guthrie, who spoke of his zeal, accuracy, and ingenuity as of the greatest service in carrying out experiments embodied in his second memoir on "Salt Solutions and Attached Water." For a part of the year 1873, however, Mr. Cowper acted as chemist to the Sewage Company under the direction of the late Major-General Scott. In 1875, he went as chemist to the Tredegar Iron Works, where he remained until 1878. In 1879, he was appointed Demonstrator to Dr. H. Debus, F.R.S., Professor of Chemistry at the Royal Naval College, Greenwich, a post which he held for five years. Amongst his arduous and important duties at Greenwich, Mr. Cowper found time to make and publish the following researches in the Transactions of this Society:—

(1.) "*The Action of Alcohol on Mercuric Nitrate*," Trans., 1881, p. 242).—The main conclusion arrived at is that one of the products of the action is the formation of a compound base containing acetylene, mercury, and mercuric oxide; the nitrate and oxalate of this base were examined."

(2.) "*On the Solubility of Glass in certain Reagents*," Trans., 1882, p. 254.—In this research, Mr. Cowper showed that aqueous solutions of ammonia and sulphide of ammonium have at 100° a considerable solvent action even on hard glass. He found that in both cases the maximum solvent power was reached at a certain degree of dilution.

(3.) "*Analysis of a Piece of Oxidised Iron from the Condenser of H.M.S. 'Spartan,'*" Trans., 1882, p. 258.—This is a study of the action of warm (*circa* 38° C.) sea-water on such iron as this condenser was made of. Perhaps the most interesting feature in this research is the very large (42·33 *per cent.*) proportion of ferrous oxide in comparison with ferric oxide (2·21).

(4.) "*On the Action of Chlorine on certain Metals*," Trans., 1883, p. 153.—This short research, the continuation of which Mr. Cowper was contemplating at the time of his death, was on that most important and little studied chapter of the interaction of the pure elements. Although the ground had been broken before, and although researches subsequent to his have contributed to our knowledge in this matter, Mr. Cowper's experiments will always be of great interest and value.

In 1884, Mr. Cowper left Greenwich, and occupied the post of Superintendent of the Education Section of the Health Exhibition. Under the presidency of Lord Reay, he, as Secretary to the Committee of Organization, conducted the work of the Educational

Conference, and subsequently edited, with great ability, the "Proceedings of the International Conference on Education" (Clowes and Sons, 4 vols., 1884).

In 1885, he was appointed Chief Clerk to the Central Institution of the City and Guilds of London, which appointment he held up to the date of his death.

An indefatigable worker, and of a most genial, helpful, and devoted disposition, Mr. Cowper, while inheriting from his father's side the distinctly scientific bent of his character, derived from that of his mother his unusual artistic taste and skill.

After a brief illness, Mr. Cowper died of acute pleurisy on the 9th of May, 1886, at the age of thirty, leaving a widow and child and many friends to lament his loss.

HENRY SUGDEN EVANS, born in 1830, was educated at the Merchant Taylors' School and the Pharmaceutical Society's School in Bloomsbury Square, London. He was the author of several papers on subjects connected with Chemistry and Pharmacy read before the British Pharmaceutical Conference and the Liverpool Chemists' Association, and was President of the Pharmaceutical Society in 1869–70.

Having settled in Canada about ten years ago, he was offered in 1884 the appointment of Chief Analyst to the Commission, an office which he held at the time of his death on the 25th February, 1887.

Mr. GEORGE HIRST, a native of Sheffield, was born January 16th, 1856. At the age of fourteen he became a pupil teacher in one of the foremost Church day schools in that town, and before the end of his apprenticeship he gained a 1st Class Queen's Scholarship, and entered Cheltenham Training College in January, 1874. During his two years' residence there, he earned the esteem and confidence of the College authorities, acting as monitor over an important section during most of his last year there; at the annual examinations, he occupied a prominent position. Early in his career, he showed a strong taste for Science, and as soon as his College training was completed, he took charge of a small school near Sheffield, so as to have time to advance his education in that direction. He attended the classes in Chemistry and Physics at Firth College, Sheffield, and gained the high commendation of the Professors for the devotion to his work and the ability he displayed.

On the opening of the Central Higher School by the Sheffield School Board with the object of dealing with the more talented pupils drawn from other Elementary Schools in the town, Mr. Hirst was appointed as a member of the staff of teachers specially selected for dealing with the advanced instruction which it was proposed to give. Here he remained until his death, and during these six years he was principally engaged in the science department taking a share in the Chemistry work until 1875, when Mr. Ripper, the Science master, was appointed to a Professorship in the Technical School affiliated to Firth College. Mr. Hirst was then appointed the teacher of Chemistry in the School—the whole of that department being under his supervision. The Laboratory will accommodate 108 students, and about 250 advanced pupils do practical work. Mr. Hirst also conducted large and successful evening classes in Chemistry and Physics. He died from the effects of a cold which was neglected until too late.

Mr. E. R. **Southby**, M.R.C.S., was born at Bridgewater, May 12th, 1833. He studied for the medical profession at King's College, London, and took his degree of M.R.C.S. in 1855, but did not practise. He was for two years, 1856–58, in Canada engaged in brewing and distilling, and afterwards was for some years with Messrs. S. Allsopp and Sons, Burton-on-Trent, both in the laboratory and brewhouse. Subsequently he undertook the management of the Wareham Oil and Candle Works at Wareham, Dorset, which were established when this industry was comparatively in its infancy, and his untiring and intelligent exertions in developing and improving the processes of the manufacture of the various products of coal oils, assisted greatly both in improving their manufacture and in economising the cost. Owing principally to the situation of the works in Dorset being unsuitable for the supply of oils at remunerative rates they were given up, and a new company under the name of the North British Oil and Candle Works was formed for the erection of works at Lanark, N.B., to work the Keyside Cannel Coal. These works, erected under the superintendence of Mr. E. R. South by and his brother, Mr. A. G. Southby, C.E., at a cost of over £25,000, were very far in advance of any in existence both in respect to the plans of the building and the plant. Through his skill, many great improvements were made in the quality of products, and the cost of manufacture greatly diminished. On relinquishing his post as manager at Lanark, after four years' good scientific and useful work, he started in 1874 in London as Analyst and Consulting Chemist, and from that time up to his death devoted his whole time to Chemistry, more particularly that connected with brewing. His highly inventive genius enabled him to make numerous improvements both in the appliances and in the materials connected with this important industry

He was appointed Analyst to the County Brewers' Society in 1882, and held the post until his death.

Died March 25th, 1886, at his residence, 101, South Hill Park, Hampstead.

Publications.—"Brewing Practically and Scientifically Considered," 1877; "Brewery Tables;" "Practical Brewing," 1885; and numerous contributions to the contemporaneous press.

Mr. FREDERICK SEAR was born at Islington on the 31st July, 1855, and on leaving school became laboratory boy to the late Dr. Stenhouse; as he was intelligent, and had a great liking for chemistry, he was sent, at the age of 16, by Dr. Stenhouse to attend the evening lectures in Chemistry and Physics at King's College, and at the same time received a thorough practical training in analytical chemistry in Dr. Stenhouse's laboratory at Pentonville under the present Editor of this Journal. He subsequently became assistant to Dr. Stenhouse and Mr. Groves, with whom he remained until he was appointed Assistant Chemist in the works of Price's Candle Company at Battersea; he remained in the service of the company until his untimely death from consumption on the 8th November, 1886. He was married in June, 1878, and leaves a widow and three children to mourn his loss.

Mr. Sear was a most skilful and painstaking analyst, and all his work was characterised not only by the neatness and care with which it was performed, but by its thoroughness. He was endowed with an ingenious and inventive mind, which displayed itself not only in the assistance he rendered in carrying out the investigations published jointly by Dr. Stenhouse and the Editor, but subsequently, when his attention was directed to technical matters, in improvements connected with the candle manufacture and saponification of fats. Patents for these new processes were taken out by him in conjunction with Mr. Rumble, Chemist to Price's Candle Company, and have been extensively employed by the Company. The Society has a lasting memorial of the painstaking and careful way in which he did all his work in the indexes of the Journal of the Society during the past five years; the Editors have a grateful remembrance of the valuable assistance he rendered in the laborious task of preparing these for the press. Mr. Sear was a good French scholar, and had a fair knowledge of German.

HENRY HOUGH WATSON, the eldest son of the late John Watson, chemist and druggist, of Bolton-le-Moors, was born on the 19th of February, 1810, and died on the 15th of August, 1886.

Although when young he was far from strong physically, he showed great perseverance; he was of an enquiring turn of mind, and had a very retentive memory. At the age of six, he entered the Bolton

Grammar School, a requisite qualification for those about to enter being that they should be able to read fluently. At this school, under the tuition of the Rev. William Allen, M.A., he acquired a comprehensive knowledge of the Latin and Greek Classics, which in later life he improved by private study, and was always a source of much pleasure to him. The close reading which he regularly pursued in order to keep up with the advance in science, so affected his eyesight that it gradually became very defective from a form of amaurosis, which latterly rendered walking alone difficult, if not dangerous. The brutal floggings, often undeserved, which he frequently witnessed during his school days, had imbued him with such an unsatisfactory opinion of schools and schoolmasters, that he had all his children taught under his own roof.

After leaving Bolton Grammar School in 1827, being then 17 years of age, he became a pupil of John Dalton, at Manchester. After studying under Dalton for four years, he obtained a certificate of competency on December 7th, 1831. During part of this time he was accompanied by his younger brother, William Barnett Watson, who also showed an early liking for chemical research (see Dalton on "Constitution of Atmosphere," *Phil. Trans.*, Part II, 1837), and who was of great assistance to the deceased throughout his professional career.

Watson displayed many of Dalton's characteristics, both socially and professionally, and for Dalton his respect and admiration never abated. His sitting-rooms were hung with framed specimens of Dalton's writing, and with numerous engravings of his illustrious teacher at various ages. He may be said to have commenced his profession as an Analytical Chemist at the age of 21 years, under his father's roof at Manor Street, Bolton, where he was born. His earliest communication to the press appeared in the *Bolton Chronicle* of July 7th, 1832, at the time of an outbreak of cholera in Bolton. In it he pointed out the importance of the use of "chloride of lime" as a disinfectant. In addition to the disinfection of articles of clothing by washing them in dilute solutions of it, he recommended that, in cholera cases, the body after death should be washed with the same solution.

As an analyst, he soon made great progress, his abilities securing for him many important engagements. For many years he was professionally engaged to conduct analyses in cases of alleged poisoning, and he had great experience as a toxicologist. His private correspondence with Dr. A. Swaine Taylor, Dr. Christison, and other eminent scientists on this and kindred subjects, forms a most interesting commentary on the progress of analytical chemistry between the years 1835 and 1860.

He was elected a Fellow of the Chemical Society in 1837, and was appointed on several Committees of the British Association, as well as being an occasional Member of the Councils of the Chemical Section. His numerous contributions to the scientific journals indicate a rare capacity for chemical research, and his other investigations show that his attention was early directed to the practical exposition of the public questions of the day. For many years Mr. Watson was Gas Examiner to the Bolton Gas Company and to the Corporation of Bolton. He originated and used a process for determining by chemical examination the illuminating power of coal-gas. The details of the process have never been published, but its accuracy was verified by frequent comparisons with photometric tests taken at the same time; by a simple calculation the illuminating power of the gas could be ascertained from the chemical results, avoiding in this way the important differences in the results frequently obtained by different observers using the photometric method. Mr. Watson was called on to examine periodically the gas of various towns. Most of the streams of the north of England appeared to have come under Mr. Watson's investigation, from time to time, during upwards of 60 years, so that a valuable record remains of the gradual and increasing pollution of streams in the districts referred to. He was selected as analyst in nearly all the original water schemes of the Lancashire towns. In arbitration cases, and before Parliamentary Committees, where the quality of water or gas was in question, the deceased was a prominent witness. He was the patentee of several valuable chemical improvements in the Arts and Manufacturers. One of the most successful was that for the Bleaching of Tallow and other Fats by permanganates. For several years before his death, Mr. Watson had discontinued the practice of his profession.

For about 55 years he regularly made monthly determinations of the rainfall and evaporation at Bolton, and since 1863, at Braystone, Cumberland, where for several years he chiefly resided, having purchased an estate there, and where he died, on the 15th August, 1886, leaving two sons, John Dalton Watson and William Henry Watson. He was placed on the Commission of the Peace for the County of Cumberland in the year 1867, and for several years acted as Chairman of the Bench of Magistrates at Whitehaven.

He married January, 1832, Miss Jane Atkinson, of Sellafield, near Whitehaven, who died on the 3rd October, 1883.

The following are some of the Papers published by the deceased, given in order:—

"On Sulphate of Barytes in Cannel;" *Phil. Mag.*, vol. 8.

"On the Absorption of Water by Efflorescent Salts;" *Phil. Mag.*, III Series, vol. 12.

"On an Extraordinary Depression of the Barometer;" *Phil. Mag.*, III Series, vol. 22.

"On the Quantity of Carbonic Acid in the Atmosphere;" *Brit. Assoc. Reports*, IV.

"On the Use of Lezlie's Hygrometer with a New Scale;" *Brit. Assoc. Reports*, IV.

"On the Phosphate and Pyrophosphate of Soda;" *Brit. Assoc. Reports*, VI.

"On the Presence of Arsenic in Sulphuric Acid;" *Med. Gaz.*, Feb. 19, 1841.

"Experiments and Observations on the Efflorescing Properties of some Salts of Soda;" *Man. Lit. and Phil. Soc. Proc.*, II Series, vol. vi.

"On Detecting the Presence of Arsenic, particularly in Reference to the Employment of Marsh's Test;" *Med. Gaz.*, Feb., 1841, and June, 1842.

"On the Tests for Strychnia and Brucia;" *Med. Gaz.*, June 14th, 1856.

"On Testing for Antimony and Arsenic by Reinsch's Process;" *Med. Gaz.*, June 20th, 1857.

WALTER WELDON[*] was born at Loughborough on the 31st October, 1832, which place he left for London in 1854. During the first six years of his London life he was engaged in literary work, among which may be mentioned the starting of a newspaper called the "Dial," which was incorporated ultimately with the "Morning Star." At a later period in 1860 he produced a periodical published monthly under the title of "Weldon's Register of Facts and Occurrences in Literature, Science, and Art," which contained articles on scientific subjects and reviews of the latest published scientific books. Among some of the early papers in it, may be noticed one on Mr. Darwin's then recently published work on the "Origin of Species." It was followed by others on "Building Stones, why they Decay;" "Recent Elementary Books on Geology," "Spectrum Analysis," "Philosophy of Earthquakes," "The Coal and Guano Dyes," &c., &c. Among the contributors of the more purely literary and artistic papers were Mr. G. A. Sala, Mr. Edmund Yates, Mr. Tegetmeier, Mr. Hollingshead, Mr. W. M. Rossetti, Mr. J. Hain Friswell, Mr. Percy Greg, and others who have since become more or less widely known by their writings. The "Register" was continued for some three years, but it may be doubted whether, at any time, it secured commercial success. The price at which it was issued made it necessary that the sale should be very large, and this probably was never the case. Finally, and fortunately for chemical technology, it had to be abandoned.

---

[*] This obituary should have appeared amongst the obituary notices for 1885-86, but was too late for insertion.

In 1865 Mr. Weldon turned his attention to the introduction and improvement of industrial chemical processes; the first of which appear to be two processes for the manufacture of the metals magnesium and aluminium. For the first, Weldon proposed heating together magnesia and iodide of sodium, whereby a double iodide was produced, which was said to be easily decomposed by sodium, or even by lead, with production of metallic magnesium. The second suggestion was to flux cryolite with chloride of calcium, and to use this mixture as a source of aluminium, instead of the more expensive chloride required for Deville's process. In 1866, the first experiments in connection with what is now known as the "Weldon process" were made at Walker in the works of the Walker Chemical Company; these, however, were abandoned at that place, but were soon after resumed at the works of Messrs. Gamble and Sons at St. Helen's, where the process was finally perfected. It was not, however, until some time in 1869 that the process was worked on a manufacturing scale. Mr. Weldon himself said (*Newcastle Chronicle* of July 5th, 1884): "The first experiments, other than laboratory experiments, with what is now known as 'the Weldon process,' were made at Walker, in the demolished works of the Walker Chemical Company, about the year 1866. After having reached a certain point, the experiments at Walker were abandoned for various reasons. They were soon afterwards resumed at the works of Messrs. J. C. Gamble & Sons, at St. Helen's, Lancashire, and it was there that the process was finally worked out." With regard to the discovery of the chemical reactions and their utilisation, which led to the Weldon process, we have a full description from Mr. Weldon's own pen in the *Journal of the Society of Chemical Industry*, 1885, p. 525, as well as a foreshadowing of further problems for future working out, should life have been spared to him. As is well known to all chemists, great economy of material was effected by Mr. Weldon's efforts, the recovery of manganese originally discharged from the chlorine works reaching as high as 90 to 95 per cent., and the price of bleaching powder being reduced by about £6 per ton. As M. Dumas, the great French chemist, observed in his address when presenting to him the gold medal of the Société d'Encouragement, "By Mr. Weldon's invention, every sheet of paper and every yard of calico has been cheapened throughout the world."

Besides the work done by Mr. Weldon in connection with his numerous patents in the industrial branch of chemistry, he kept himself well informed as to the more recent work in the department of pure science; to which he contributed several papers on theoretical questions, as may be seen in his papers on the "Periodic Law" and on the "Ratios one to another of the Atomic Weights of the Elements."

Mr. Weldon's scientific achievements were fully recognised both in England and on the Continent. He was made a Chevalier of the Legion of Honour by the French Government, and received the Great Medal from the Société d'Encouragement presented to him on behalf of the Society, by the veteran French chemist, M. Dumas. In England, Mr. Weldon was a Fellow of the Chemical and Royal Societies, and of the Institute of Chemistry; but especially will his name be long known as one of the most energetic members of the Society of Chemical Industry, in the foundation of which he took a leading part, and of which Society he held the Presidentship during the years 1883–84. In connection with this latter Society, it may be remarked that when some difficulty occurred in connection with the "Abstracts of Patents" published in the Journal, Mr. Weldon, in addition to his other multifarious duties, took upon himself the abstraction and carried it out for a considerable time. Besides the vast labour and anxieties entailed by the writing, technological researches, &c., involved in the invention and maintenance of the numerous patents bearing his name, or taken out jointly with others, Mr. Weldon kept fully abreast with the advance in inorganic chemical science; and he occasionally contributed papers, which always contained something of original thought, and were always interesting and suggestive. At the meetings of the British Association in Montreal, he contributed a paper on the "Periodic Law," and shortly before his death he published for private circulation a work "On the Ratios, one to another, of the Atomic Weights of the Elements," Chapter I. This Chapter I being devoted to "The Glucinium Family."

To his scientific attainments he united, as may indeed be inferred, singular literary skill; and there was perhaps not another man in England who could make a difficult matter more plain to people of ordinary intelligence, and that without the least sacrifice of accuracy.

Mr. Weldon was a man of the simplest personal habits combined with great generosity to others, and a frank and genial bearing to people of all ranks. He possessed much tact and delicacy of feeling, which pointed out to him the directions in which his kindness might reach others, and his practical nature enabled him instinctively to seize the proper moments for its exercise. He was, moreover, a man of extraordinary energy and perseverance, united to a thorough knowledge of the world and great business capacity; and to these he was largely indebted for the rapid and successful adoption of his inventions. He spared no pains, and neglected no details. In addition, he had made himself more or less familiar with numerous branches of chemical industry, and in the alkali trade he was regarded as an expert to whose opinion very great value was attached.

His supreme delight appeared to be in the grounds and gardens surrounding his country place, Rede Hall, Suffolk, on which he had spent much money and in which he took great interest.

Mr. Weldon suffered much during his life from neuralgia, probably much increased by long railway journeys undertaken in the interests of his company; but the final cause of his death was an attack of heart disease in September, 1885, after attending the meeting of the British Association at Aberdeen.

XLVII.—*Dehydracetic Acid.*

By W. H. PERKIN, Jun., Ph.D.

DEHYDRACETIC acid was first prepared by Geuther in the year 1866, who obtained it by passing a current of carbonic anhydride over the sodium compound of ethylic acetoacetate. From the analyses of the acid itself and also of its barium and sodium salts, Geuther showed that this new compound was a monobasic acid of the formula $C_8H_8O_4$. He supposed it to be formed by the dehydration of acetic acid, probably thus—

$$4CH_3{\cdot}COOH = C_8H_8O_4 + 4H_2O,$$

hence the name dehydracetic acid.

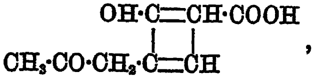
Geuther does not appear to have examined this acid further, and it is to Oppenheim and Precht (*Ber*, 9, 324) that the first careful study of it is due. These chemists showed that when dehydracetic acid is treated with alkalis it is decomposed into acetone, acetic acid, and carbonic anhydride, thus:—

$$C_8H_8O_4 + 3H_2O = CO_2 + CH_3{\cdot}CO{\cdot}CH_3 + 2CH_3{\cdot}COOH.$$

Besides these products, they obtained by the hydrolysis of dehydracetic acid with baryta-water a small quantity of a crystalline substance very much resembling orcinol, and this led Beilstein to place dehydracetic acid in the aromatic series (*Handbuch der organischen Chemie*, 1527—1528).

Oppenheim and Precht also prepared the methylic and ethylic salts of dehydracetic acid, chlorodehydracetic acid, $C_8H_7ClO_4$, bromodehydracetic acid, $C_8H_7BrO_4$, and by reduction with zinc and hydrochloric acid a new acid of the formula $C_8H_{10}O_3$.

By the action of pentachloride of phosphorus on dehydracetic acid, they obtained a remarkable chloride of the formula $C_8H_6O_2Cl_2$, the formation of which led them to imagine that dehydracetic acid contained two hydroxyl-groups. For this reason they proposed the formula—



$$\begin{array}{r} \mathrm{OH{\cdot}C{=}CH{\cdot}COOH} \\ |\quad\;\; | \quad\;\;\;\;\;\;\; \\ \mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}C{=}CH} \quad\;\;\;\;\;\;\; \end{array},$$

as best representing the constitution of this acid.

At the suggestion of Wislicenus, Shibbye (*Dissertation*, Würzburg, 1882, 5), at a later date, repeated the experiments of Oppenheim and Precht on the action of alkalis on dehydracetic acid, and showed that besides acetone, acetic acid, and carbonic anhydride, considerable quantities of malonic acid were also formed.

As these results were still insufficient to definitely prove the constitution of dehydracetic acid, I thought it would be interesting to carry these experiments further, and wish now to bring before the Society the results I have obtained.

Dehydracetic acid, $C_8H_8O_4$, contains besides the carboxyl-group, two oxygen-atoms, which may either be present as CO, OH, or C·O·C.

When treated with hydroxylamine or phenylhydrazine, one oxygen-atom is easily displaced, forming the derivatives $C_7H_8O_3(CNOH)$ and $C_8H_8O_3(N_2H{\cdot}C_6H_5)$ respectively, a proof that one of the oxygen-atoms is present as CO; but all attempts to displace a second atom by the above groups were fruitless.

Dehydracetic acid does not give an acetyl-compound when treated with acetic anhydride, even after long boiling, and it is therefore clear that the fourth oxygen-atom is not present as hydroxyl, but that it is most probably united by each of its affinities to a different carbon-atom thus: C·O·C. This view is borne out by the reduction experiments of Oppenheim and Precht, as also by the behaviour of dehydracetic acid when treated with phosphorus pentachloride. In order to obtain some further clue as to the arrangement of the atoms in this interesting acid, the hydrolysis with alkalis was next very carefully studied.

In a paper on dehydrobenzoylacetic acid (Trans., 1885, 284) it was shown that when this acid is treated with alkalis, the first change which takes place is a quantitative decomposition into 2 mols. of benzoylacetic acid, thus:—

$$\underset{\text{Dehydrobenzoyl-acetic acid.}}{C_{18}H_{12}O_4} + 2H_2O = \underset{\text{Benzoylacetic acid.}}{2C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COOH.}$$

This result is very important for two reasons:—*Firstly*, it shows that the dehydrobenzoylacetic acid is really formed by the splitting off of 2 mols. of water from 2 mols. of benzoylacetic acid; and *secondly*, it proves that the two C_6H_5-groups are intact in the dehydrobenzoylacetic acid, and that all changes which take place in its formation from benzoylacetic acid must take place within the group —$CO{\cdot}CH_2{\cdot}COOH$. In determining the constitution of dehydracetic acid, it was clearly just as important to determine whether it contained two methyl-groups, in which case the formula proposed by Oppenheim and Precht would be incorrect.

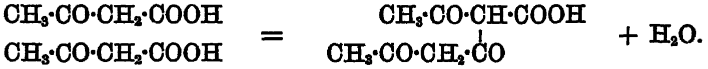
If dehydracetic acid be very carefully hydrolysed with potash, it is possible to isolate an acid, which is without doubt acetoacetic acid; although naturally owing to the instability of the latter no quantitative experiments could be made. From this result, it is legitimate to suppose that this acid, when treated with potash, in a way exactly analogous to dehydrobenzoylacetic acid, is first split up into 2 mols. of acetoacetic acid, thus:—

$$C_8H_8O_4 + 2H_2O = 2CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH.$$

This being the case, it is clear that dehydracetic acid must contain two methyl-groups, in the same way as dehydrobenzoylacetic acid contains two phenyl-groups.

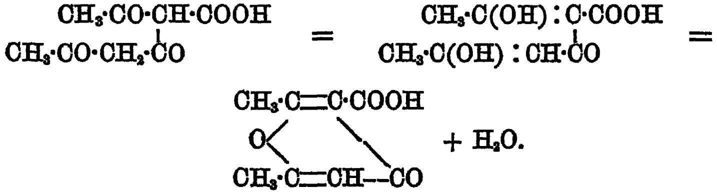
The next question is: How is dehydracetic acid formed from 2 mols. of acetoacetic acid?

Dehydracetic acid being a monobasic acid, it naturally follows that one of the carboxyl-groups of one of the molecules of acetoacetic acid must take part in the reaction. Now, as the methyl-groups remain intact, this change can only take place by the condensation of the carboxyl-group of one molecule with the methylene-group of the other molecule, thus:—

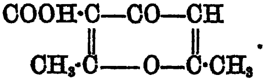


$$\begin{array}{l}CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH\\ CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH\end{array} = \begin{array}{r}CH_3{\cdot}CO{\cdot}CH{\cdot}COOH\\ |\qquad\quad\\ CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO\end{array} + H_2O.$$

In the formation of dehydracetic acid from this intermediate compound, one more molecule of water is split off; the simplest way of effecting this being thus*:—

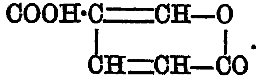


The most probable formula for dehydracetic acid would therefore be—



$$\begin{array}{l}COOH{\cdot}C—CO—CH\\ \qquad\quad\ \| \qquad\quad \|\\ \qquad CH_3{\cdot}C——O—C{\cdot}CH_3\end{array}.$$

In considering how best to obtain evidence in support of this conclusion, it struck me that there was a certain resemblance between this formula and the formula given to cumalinic acid by v. Pechmann, namely:



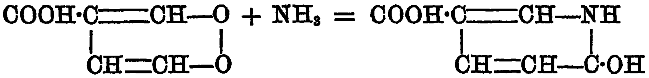
$$\begin{array}{l}COOH{\cdot}C=CH—O\\ \qquad\qquad | \qquad\quad |\\ \qquad\quad CH=CH—CO\end{array}.$$

---

* This change is fully discussed in a paper on "Dehydrobenzoylacetic Acid" (Trans., 1885, 295—297).

The striking relation of this acid to chelidonic and meconic acids did not occur to me till afterwards.

If the methyl salt of cumalinic acid is treated with ammonia, it is converted, as v. Pechmann has shown in his beautiful researches (*Ber.*, **17**, 2391), into hydroxynicotinic acid, thus:—



$$\begin{array}{l} COOH{\cdot}C{=\!=}CH{-}O \\ \quad | \qquad\quad | \\ \quad CH{=}CH{-}O \end{array} + NH_3 = \begin{array}{l} COOH{\cdot}C{=\!=}CH{-}NH \\ \quad | \qquad\quad | \\ \quad CH{=}CH{-}C{\cdot}OH \end{array}$$

Cumalinic acid. Hydroxynicotinic acid.

It was therefore possible that dehydracetic acid under similar conditions might also yield pyridine-derivatives. The experiment has shown that this is indeed the case.

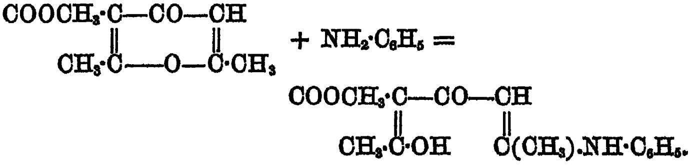
If methylic dehydracetate is treated with ammonia or aniline, reaction immediately sets in, and pyridine-derivatives are formed, the decomposition being quantitative.

The products formed by the action of ammonia I have prepared but not analysed, as, curiously enough, Haitinger, at the same time as myself, investigated the action of ammonia on dehydracetic acid, and has reserved the further study of these products.

When methylic dehydracetate is warmed with aniline, two substances, $C_{15}H_{15}NO_3$ and $C_{13}H_{13}NO$, are formed, of which the former is undoubtedly the primary product.

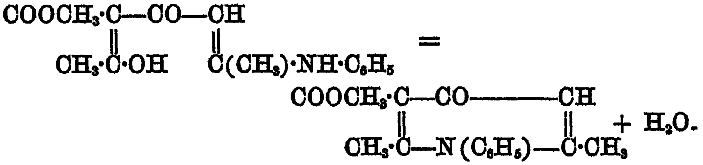
The reaction probably takes place in two stages, in a way similar to that shown by v. Pechmann in the case of the cumalinic acid.

I.



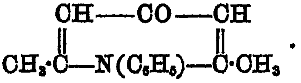
$$\begin{array}{l} COOCH_3{\cdot}C{-}CO{-}CH \\ \qquad \| \qquad\quad \| \\ CH_3{\cdot}C{-\!-}O{-}C{\cdot}CH_3 \end{array} + NH_2{\cdot}C_6H_5 = \begin{array}{l} COOCH_3{\cdot}C{-}CO{-}CH \\ \qquad \| \qquad\quad \| \\ CH_3{\cdot}C{\cdot}OH \quad C(CH_3).NH{\cdot}C_6H_5. \end{array}$$

II.

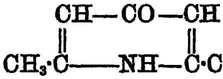


$$\begin{array}{l} COOCH_3{\cdot}C{-}CO{-}CH \\ \qquad \| \qquad\quad \| \\ CH_3{\cdot}C{\cdot}OH \quad C(CH_3){\cdot}NH{\cdot}C_6H_5 \end{array} = \begin{array}{l} COOCH_3{\cdot}C{-}CO{-\!-\!-}CH \\ \qquad \| \qquad\qquad\quad \| \\ CH_3{\cdot}C{-}N(C_6H_5){-}C{\cdot}CH_3 \end{array} + H_2O.$$

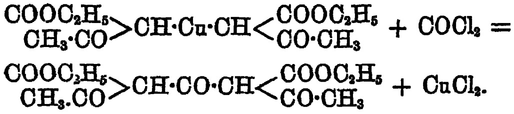
During this synthesis, partial hydrolysis of the compound $C_{15}H_{15}NO_3$ and decomposition into carbonic anhydride and the substance $C_{13}H_{13}NO$ takes place. The latter has therefore the constitution—



$$\begin{array}{l} CH{-\!-}CO{-\!-}CH \\ \| \qquad\qquad\quad \| \\ CH_3{\cdot}C{-}N(C_6H_5){-}C{\cdot}CH_3 \end{array}.$$

If the group  be termed lutidone, it follows that the primary product of the action of aniline on methylic dehydracetate is methylic phenyllutidinecarboxylate, whereas the substance $C_{13}H_{13}NO$ is phenyllutidone.

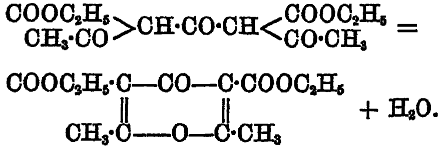
A most interesting synthetical proof of the constitution given above to dehydracetic acid has lately been carried out by Conrad and Guthzeit (*Ber.*, **19**, 19, and **20**, 151 and 154). These chemists found that when the copper salt of ethylic acetoacetate is treated with phosgene, the following decomposition takes place:—



$$\begin{matrix}COOC_2H_5\\CH_3\cdot CO\end{matrix}\!>CH\cdot Cu\cdot CH<\!\begin{matrix}COOC_2H_5\\CO\cdot CH_3\end{matrix} + COCl_2 =$$

$$\begin{matrix}COOC_2H_5\\CH_3.CO\end{matrix}\!>CH\cdot CO\cdot CH<\!\begin{matrix}COOC_2H_5\\CO\cdot CH_3\end{matrix} + CuCl_2.$$

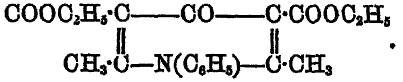
This substance does not appear to exist as such, but spontaneously loses a molecule of water, and is converted into ethylic carboxyldehydracetate thus:—



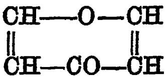
$$\begin{matrix}COOC_2H_5\\CH_3\cdot CO\end{matrix}\!>CH\cdot CO\cdot CH<\!\begin{matrix}COOC_2H_5\\CO\cdot CH_3\end{matrix} =$$

Ethylic carboxyldehydracetate.

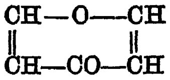
If this compound is treated with aniline, ethylic phenyllutidonedicarboxylate is found—



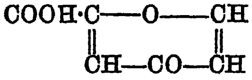
The free acid when heated to 270° is converted into phenyllutidone, a substance identical with that which I obtained by the action of aniline on methylic dehydracetate. This elegant synthesis by Conrad and Guthzeit proves without doubt that dehydracetic acid really has the formula given by me above.

The group pyrone,  (Haitinger and Zieben, *Monatsh.*, **6**, 283), besides being present in dehydracetic acid, is the basis of a number of interesting acids, among them chelidonic acid and meconic acid.

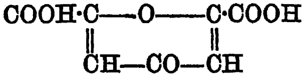
The relation of the most important representatives of this class to one another is clearly seen when their constitutional formulæ are placed side by side, thus:—



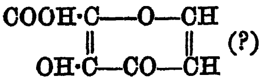
Pyrone.



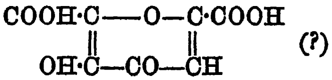
Pyronecarboxylic acid.
Comanic acid.



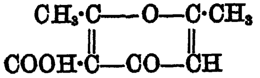
Pyronedicarboxylic acid.
Chelidonic acid.



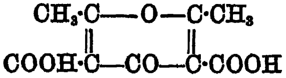
Oxypyronecarboxylic acid.
Comenic acid.



Oxypyronedicarboxylic acid.
Meconic acid.



Dimethylpyronecarboxylic acid.
Dehydracetic acid.



Dimethylpyronedicarboxylic acid.

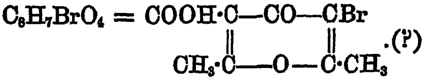
Preparation of Dehydracetic Acid.

In preparing dehydracetic acid, Oppenheim and Precht's method, which consists in passing the vapours of ethylic acetoacetate through a tube heated to dull redness, was after a few slight modifications found to give the best results.

The details of this process are the following:—A piece of combustion tube, 50 inches long, and bent about 18 inches from one end to an angle of 120°, is filled up to the bend with small pieces of pumice, and heated in a combustion furnace to dull redness. 200 grams of ethylic acetoacetate are then slowly distilled through this tube, from a distilling flask directly connected to the tube by means of a cork, and the product which comes over is collected in a well-cooled flask placed at the other end of the tube. A dark-brown oil is thus obtained, which on cooling should solidify almost entirely to a mass of crystals of dehydracetic acid. In order to isolate the acid, the crude product is rapidly distilled from a retort, until the temperature rises to 195°, and the residue is then poured into a dish and allowed to solidify. The dark-brown cake formed in this way is next broken up, and digested with an excess of a fairly strong solution of sodic carbonate and a little animal charcoal for a short time, and filtered hot. The filtrate, on cooling and acidifying with hydrochloric acid, deposits the dehydracetic acid as a slightly brownish-coloured crystalline powder, which, after being collected, well washed, and recrystallised from water is easily obtained pure.

The distillate from the crude dehydracetic acid, boiling below 195°, yields on fractioning a considerable quantity of ethylic acetoacetate, which, when again passed through the tube, gives a further quantity of acid. With a little practice it is easy to obtain by this method from 58—66 grams of pure dehydracetic acid from 200 grams of ethylic acetoacetate. Most of the dehydracetic acid used in this research was obtained from Meister, Lucius, and Brünning, through the kindness of Herr v. Gerichten, and I take this opportunity of thanking these gentlemen for their liberality.

Monobromodehydracetic Acid,



$$C_8H_7BrO_4 = \begin{array}{ccccc} COOH\cdot C & — & CO & — & CBr \\ \| & & & & \| \\ CH_3\cdot C & — & O & — & C\cdot CH_3 \end{array} .(?)$$

Monobromodehydracetic acid was first obtained by Oppenheim and Precht (*Ber.*, 9, 1101) by treating dehydracetic acid with bromine. As the yield of the brominated acid obtained by this method is small, several experiments were made with the object of improving it. The following modification was found to give good results:—

5 grams of dehydracetic acid are dissolved in about 50 grams of chloroform, a slight excess of bromine, and two or three crystals of iodine added, and the whole warmed in a water-bath at about 50° for a minute or two. As soon as the reaction has once set in, it continues at the ordinary temperature, and is usually finished in about 12 hours. The liquid is then decanted from any crystals which may have separated, and is allowed to evaporate at the ordinary temperatures in an open dish, when a slightly yellowish crystalline mass is left behind, consisting of a mixture of monobromodehydracetic acid and unchanged dehydracetic acid. These two acids may be easily separated by recrystallisation from alcohol, in which the latter is much more easily soluble than the former.

The monobromodehydracetic acid thus obtained is mixed with any crystals which may have separated from the chloroform solution during the preparation, and is purified by two crystallisations from alcohol.

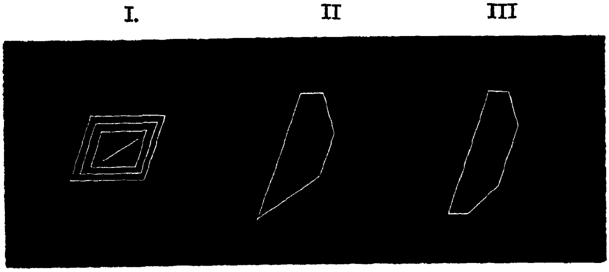
The analysis gave the following numbers:—

0·3258 gram substance gave 0·2458 gram AgBr.

	Found.	Theory. $C_8H_7BrO_4$.
Br	32·11 per cent.	32·38 per cent.

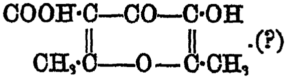
Monobromodehydracetic acid melts at 137° (Oppenheim and Precht give 134°). It is easily soluble in hot alcohol, chloroform, benzene, and light petroleum, but only sparingly in alcohol and light petroleum in the cold.

It crystallises from the hot solution in methyl alcohol, on cooling slowly, in beautiful plates and prisms, having the following forms:—



When the hot solution in methyl alcohol is rapidly cooled, curiously striated four-sided plates (I) are produced, but on slowly crystallising the forms lose the striated appearance and become well developed mostly in the forms II and III.

Hydroxydehydracetic Acid, $C_8H_7O_4{\cdot}OH$ =



$$\begin{array}{l} COOH{\cdot}C{-}CO{-}C{\cdot}OH \\ \quad\quad\;\; \| \qquad\quad\; \| \\ CH_3{\cdot}C{-}O{-}C{\cdot}CH_3 \end{array} \text{.(?)}$$

This interesting compound is the first product of the action of potash on monobromodehydracetic acid, thus:—

$$C_8H_7BrO_4 + KOH = C_8H_7O_4{\cdot}OH + KBr.$$

To prepare it, pure monobromodehydracetic acid is dissolved in a little alcoholic potash, then mixed with an excess of concentrated alcoholic potash, and the whole allowed to stand 14 days at a temperature of 35—40°. The mass which is at first quite thick, soon becomes more fluid, and at the end of the operation again thick and brownish coloured. In order to isolate the product, water and dilute sulphuric acid are added, when a solid acid separates, which is collected and well washed with water. The mother-liquors, on repeated extraction with ether, give a further quantity of this acid, which is, however, not so pure. The crude product obtained in this way is a mixture of hydroxydehydracetic acid and unchanged monobromodehydracetic acid. These two acids can be easily separated by treatment with chloroform, in which the hydroxy-acid is almost insoluble. The crystalline mass which remains undissolved is then once recrystallised from dilute alcohol, and thus obtained as a white sandy crystalline precipitate, which, on analysis, gave the following results:—

I. 0·2381 gram substance gave 0·0947 gram H_2O and 0·4535 gram CO_2.

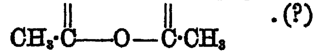
II. 0·2060 gram substance gave 0·0831 gram H_2O and 0·3927 gram CO_2.

	Found.		Theory.
	I.	II.	$C_8H_8O_5$.
C	51·95	51·99 per cent.	52·17 per cent.
H	4·42	4·48 ,,	4·35 ,,
O	43·63	43·53 ,,	43·47 ,,

Hydroxydehydracetic acid, when rapidly heated, melts at 250—255° with decomposition, if slowly heated, the acid begins to decompose and char at 210°. It is fairly soluble in hot ethyl alcohol and methyl alcohol, but almost insoluble in cold water, chloroform, light petroleum, benzene, and acetone. The hot solutions in alcohol or water deposit the acid on cooling in the form of a heavy sandy precipitate, which when examined under the microscope is found to consist of a mass of small but badly formed four-sided crystals.

The alcoholic or aqueous solution gives an intense violet coloration on the addition of a drop of ferric chloride. When carefully heated in small quantities, this acid sublimes with slight decomposition. Hydroxydehydracetic acid dissolves easily in alkalis. The silver salt appears curiously enough to have the constitution $C_8H_6O_5Ag_2$, which would point to the acid being bibasic. It is intended to further study this interesting acid, and experiments on the subject are already in progress.

Acetate of Hydroxydehydracetic Acid, $C_8H_7O_4(OC_2H_3O)$ =



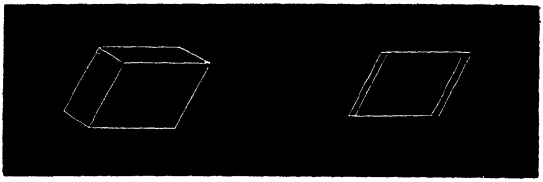
$$\begin{array}{l}\mathrm{COOH{\cdot}C{-}CO{-}C{\cdot}OC_2H_3O} \\ \quad\;\;\, \| \qquad\quad\; \| \qquad\qquad .(?) \\ \mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_3}\end{array}$$

In order to prepare this substance, a small quantity of hydroxydehydracetic acid was boiled with an excess of acetic anhydride for two hours, the bulk of the acetic anhydride distilled off, and the clear solution after cooling mixed with water. As soon as the excess of acetic anhydride had been decomposed, the whole was extracted several times with ether, the ethereal solution well washed, and allowed to evaporate at ordinary temperatures. In this way, a colourless crystalline mass was obtained, which, after washing with a little water and drying on a porous plate over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0·2155 gram substance gave 0·0885 gram H_2O and 0·4180 gram CO_2.

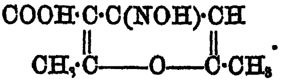
	Found.	Theory. $C_{10}H_{10}O_6$.
C......	52 90 per cent.	53·09 per cent.
H......	4·56 „	4·42 „
O......	42·54 „	42·48 „

This acetate melts at 165—167°. It is easily soluble in hot alcohol, less so in benzene, chloroform, ether, and bisulphide of carbon. From the hot solution in methyl alcohol, it separates on cooling as a hard sandy mass, which when seen under the microscope is found to consist of beautifully formed crystals, mostly having the following forms:—



When boiled with water or alcohol for any length of time, it is slowly decomposed, hydroxydehydracetic acid being apparently regenerated. The acetate gives no coloration with ferric chloride. When heated in a test-tube, acetic anhydride is split off, and a small quantity of a white sublimate is obtained, which gives a violet coloration with ferric chloride, and consists therefore probably of regenerated hydroxydehydracetic acid.

Oxime of Dehydracetic Acid,



$$\begin{array}{l} COOH\cdot C\cdot C(NOH)\cdot CH \\ \quad\quad\quad \| \quad\quad\quad\quad\quad \| \\ CH_3\cdot C—O—C\cdot CH_3 \end{array}.$$

Dehydracetic acid combines readily with hydroxylamine, if its sodium salt be allowed to remain in contact with a solution of this compound. In a short time, a crystalline substance begins to separate, and after standing for 24 hours the reaction is complete. In order to isolate the product, the solution is slightly acidified with dilute sulphuric acid, and the precipitate thus thrown down is collected, washed with water, and repeatedly recrystallised from alcohol or dilute acetic acid, or light petroleum. In this way, colourless needles are obtained, melting at about 171—173° with decomposition.

Analysis:—

0·1874 gram substance gave 0·0812 gram H_2O and 0·3640 gram CO_2.

0·2261 gram substance gave 15·5 c.c. N, $t = 15°$, bar. = 720 mm.

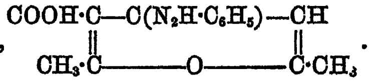
	Found.	Theory. $C_7H_8O_3CNOH$.
C	52·97 per cent.	52·46 per cent.
H	4·81 „	4·92 „
N	7·60 „	7·65 „
O	34·62 „	34·97 „

This substance is formed from dehydracetic acid according to the equation—

$$C_8H_8O_4 + NH_2 \cdot OH = C_9H_8O_3(NOH) + H_2O.$$

This oxime is easily soluble in alcohol, benzene, and acetic acid, but only sparingly in cold light petroleum. The alcoholic solution gives an intense violet coloration with ferric chloride. Odernheimer (*Ber.*, **17**, 2087) has also prepared the oxime of dehydracetic acid. In addition to the properties given above, he found that the alcoholic solution was precipitated by silver nitrate, an unstable white precipitate of the silver salt being formed. He also prepared a barium salt by precipitating a neutral solution of the oxime with baric chloride.

Phenylhydrazinedehydracetic Acid,



$$\begin{array}{l} COOH \cdot C — C(N_2H \cdot C_6H_5) — CH \\ \quad \| \qquad\qquad\qquad\qquad\qquad \| \\ CH_3 \cdot C ——— O ——— C \cdot CH_3 \end{array}.$$

The phenylhydrazine-derivative of dehydracetic acid may be prepared in several ways. It was first obtained by treating the sodium salt of dehydracetic acid with a solution of phenylhydrazine acetate, and then acidifying with dilute sulphuric acid, but the easiest way of preparing it is to add an excess of phenylhydrazine to the warm alcoholic solution of dehydracetic acid, and then allowing it to stand. In a short time, a yellow crystalline solid separates out, which after collecting, well washing with alcohol, and recrystallising from alcohol, is easily obtained pure.

Analysis:—

0·2069 gram substance gave 0·1041 gram H_2O and 0·4940 gram CO_2.

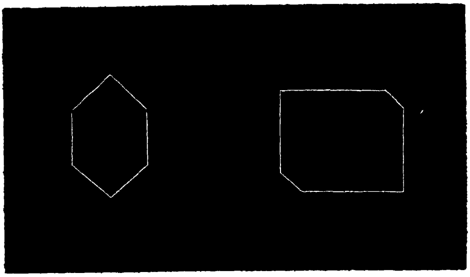
0·2634 gram substance gave 26 c.c. N, $t = 18°$, bar. = 719 mm.

	Found.	Theory. $C_8H_8O_3N_2H \cdot C_6H_5$.
C	65·12 per cent.	65·12 per cent.
H	5·59 „	5·42 „
N	10·79 „	10·85 „
O	18·50 „	18·61 „

This substance is formed from dehydracetic acid according to the equation—

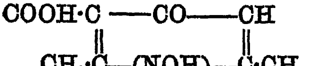
$$C_8H_8O_4 + NH_2\cdot NH\cdot C_6H_5 = C_8H_8O_3\cdot N_2H\cdot C_6H_5 + H_2O.$$

When rapidly heated, it melts at 207° with decomposition, but when slowly heated it begins to decompose at 200°. It is moderately easily soluble in hot benzene, alcohol, and chloroform, but only sparingly in light petroleum. From the hot solution in benzene or alcohol, it crystallises on cooling in beautiful brilliant yellow crystals, which when examined under the microscope are found to have the following forms:—



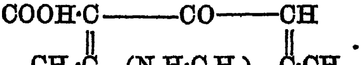
It dissolves with difficulty in ammonia and sodic carbonate solutions, and is reprecipitated by acids apparently unchanged.

Haitinger (*Ber.*, 18, 453) suggests that these products of the action of hydroxylamine and phenylhydrazine on dehydracetic acid may have constitutions different from those given above. He thinks it very probable that these basic substances may have acted in the same way as ammonia, producing compounds of the constitution—



$$\begin{array}{l} COOH\cdot C — CO — CH \\ \qquad \| \qquad\qquad\qquad \| \\ CH_3\cdot C—(NOH)—C\cdot CH_3 \end{array}$$

and



$$\begin{array}{l} COOH\cdot C — CO — CH \\ \qquad \| \qquad\qquad\qquad\qquad \| \\ CH_3\cdot C—(N_2H\cdot C_6H_5)—C\cdot CH_3 \end{array}.$$

This is quite possible, although improbable, and I hope by further experiments to be able to distinguish between these formulæ.

Action of Potash on Dehydracetic Acid.

In the introduction to this paper, I mentioned that the first change which dehydracetic acid underwent when treated with potash was decomposition into 2 mols. of acetoacetic acid, thus:—

$$C_8H_8O_4 + 2H_2O = 2CH_3\cdot CO\cdot CH_2\cdot COOH.$$

The experiments which were made to prove this were conducted in the following way:—

Pure dehydracetic acid was first dissolved in a little dilute alcoholic potash, then an excess of a concentrated alcoholic potash solution added, and the whole allowed to stand for 14 days. The mass soon became brownish coloured and quite thick, but towards the end of the reaction it was again more fluid. The thick stage appears to be brought about by the separation of the potassium salt of dehydracetic acid; this at a later stage gives place to the potassium salt of acetoacetic acid, which is much more soluble.

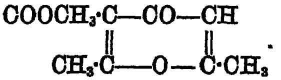
In order to isolate the product of the reaction, the whole is dissolved in water, acidified with dilute sulphuric acid, and filtered from any unchanged dehydracetic acid which may separate out. The filtrate is then extracted several times with ether, the ethereal solution washed with water, dried over calcic chloride, and evaporated at as low a temperature as possible. A small quantity of dehydracetic acid, which generally crystallises out during this operation, can be easily removed by treating the residue with a small quantity of water and filtering, when the dehydracetic acid remains undissolved. The filtrate which contains the acetoacetic acid gives the characteristic violet coloration on adding ferric chloride. If this solution be extracted with pure ether, a small quantity of a yellowish-coloured oil is obtained, which shows all the reactions of acetoacetic acid. In order to obtain it as pure as possible, it was allowed to stand for some time over sulphuric acid in a vacuum, and then further characterised by distilling with water. In this way, carbonic anhydride was evolved and a distillate obtained, which, when treated with orthonitrobenzaldehyde and dilute soda, gave the indigo reaction very distinctly, thus proving the presence of acetone. The acetoacetic acid had been decomposed into carbonic anhydride and acetone thus:—

$$CH_3\cdot CO\cdot CH_2\cdot COOH = CH_3\cdot CO\cdot CH_3 + CO_2.$$

The quantity of acetoacetic acid obtained in this way is naturally very small, owing to its instability.

It is an interesting fact that Conrad and Guthzeit (*Ber*, **20**, 152) also obtained a substance by the action of potash on ethylic dimethylpyronedicarboxylate, which gave a violet coloration with ferric chloride. They consider it probable that in this case acetoacetic acid was also produced by the hydrolysis.

Methylic Dehydracetate,



$$\begin{array}{l} COOCH_3\cdot C—CO—CH \\ \qquad\quad \| \qquad\quad\ \ \| \\ CH_3\cdot C—O—C\cdot CH_3 \end{array}.$$

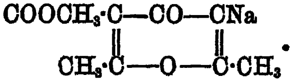
The methylic ether of dehydracetic acid used in the following experiments was prepared by Oppenheim and Precht's method (*Ber.*, **9**, 324), that is, by treating the silver salt of dehydracetic acid with methyl iodide, and extracting the product with ether. The yield obtained in this way is far from satisfactory, owing to the difficulty of preparing the silver salt in a pure condition, but up to the present I have not been able to improve on this method, the ordinary methods of etherification with alcohol and hydrochloric acid, &c., being useless in the case of dehydracetic acid. It is, however, very essential, in preparing this methylic salt from the silver salt, to have all the materials scrupulously dry, otherwise no methylic salt at all is obtained.

Methylic dehydracetate melts at 91°, as Oppenheim and Precht have shown. In experimenting with it, I have found it to possess most remarkable properties. It is easily soluble in water, producing a solution which has a decidedly acid reaction to litmus-paper. When treated with potash it is instantly saponified, even in the cold. If a solution of methylic dehydracetate (1 mol.) in pure dry ether is mixed with an ethereal solution of sodic ethylate (1 mol.), a pink sodium compound is precipitated, which, after being collected, well washed with ether, and dried over sulphuric acid in a vacuum, gave the following numbers on analysis :—

I. 0·1440 gram substance gave 0·0476 gram Na_2SO_4.
II. 0·2414 „ „ 0·0788 „

	Found.		Theory.
	I.	II.	$C_8H_6(Na)O_4CH_3$.
Na......	10·71	10·60 per cent.	11·27 per cent.

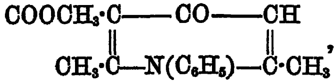
It is possible that this sodium compound has the formula



$$\begin{array}{c} COOCH_3\cdot C—CO—CNa \\ \| \qquad\quad \| \\ CH_3\cdot C—O—C\cdot CH_3 \end{array}.$$

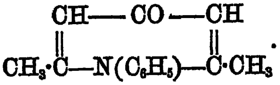
The hydrogen-atom of the CH-group in methylic dehydracetate may, on account of its position between the ketone-group —CO— and the ether-group $\equiv C—O—C\equiv$, have an acid character like the hydrogen-atoms of the CH_2-group in ethylic acetoacetate. It does not appear possible, however, by acting on ethylic or methylic dehydracetate with ethyl iodide to obtain substituted dehydracetic acids (see Shibbye, *Inaugural Dissertation*, Wurzbürg, 1882, page 12), for this the sodium compound is too unstable. The sodium compound dissolves easily in water, forming a pinkish-coloured solution. On quickly adding acid to this and extracting at once with ether, I once succeeded in obtaining colourless crystals melting at 85—90°, and which consisted probably of impure methylic dehydracetate. On repeating this experiment several times, however, I have since always obtained an uninviting brownish resin, which resisted all attempts to get it in a crystalline form.

Methylic Phenyllutidonecarboxylate,



$$\begin{array}{l} COOCH_3\cdot C\text{——}CO\text{——}CH \\ \quad\quad\quad\;\; \| \quad\quad\quad\quad\quad\quad \| \\ \quad\; CH_3\cdot C\text{—}N(C_6H_5)\text{—}C\cdot CH_3 \end{array},$$

and Phenyllutidone,



$$\begin{array}{l} CH\text{——}CO\text{——}CH \\ \| \quad\quad\quad\quad\quad\quad \| \\ CH_3\cdot C\text{—}N(C_6H_5)\text{—}C\cdot CH_3 \end{array}.$$

Methylic dehydracetate when treated with aniline is converted almost immediately into methylic phenyllutidonecarboxylate and phenyllutidone, as described in the introduction. In order to effect this change, pure methylic dehydracetate dissolved in a little methyl alcohol, is mixed with about twice its weight of aniline, and warmed gently for about 15 seconds to 50°. An equal bulk of water is then added, and the whole allowed to stand in a cool place for 12 hours. At the end of this time, it is found that a small quantity of a substance crystallising in long, colourless needles has separated. This, after collecting, washing with water, and once recrystallising, is easily obtained pure.

The analysis gave the following numbers:—

0·1472 gram substance gave 0·0775 gram H_2O and 0·3750 gram CO_2.

	Theory. $C_{15}H_{15}NO_3$.	Found.
C	70·04 per cent.	69·66 per cent.
H	5·83 „	5·69 „

Methylic phenyllutidonecarboxylate is insoluble in sodic carbonate solution. On boiling with alcoholic potash, it is easily saponified, a colourless acid being produced, which has, however, not yet been further examined.

The principal product of the action of aniline on methylic dehydracetate is, however, not methylic phenyllutidonecarboxylate, but a substance which remains dissolved in the mother-liquor after this has crystallised out. If these mother-liquors are evaporated on a water-bath, the solution becomes yellower and yellower, and at last quite deep orange-coloured. This is due to the formation of a colouring matter, and if the evaporation is carried on to dryness, a reddish amorphous mass with a magnificent green lustre remains, which appears to be this colouring matter in an almost pure state. No attempt has been made to isolate and purify this substance, owing to the small amount of material at command.

In order, however, to avoid the formation of this colouring matter, the solution was first acidified with dilute hydrochloric acid, and then evaporated almost to dryness on a water-bath. The yellow colouring matter does not appear to be formed when acid solutions are employed, the residue left on evaporation being an almost colourless syrup, which did not crystallise after standing for some hours. The whole was therefore rendered slightly alkaline by the addition of potash solution and allowed to stand in a cool place for some hours. After about six hours, a quantity of needle-shaped crystals had separated, which, when collected, washed with a little water, and recrystallised from this solvent, were easily obtained pure.

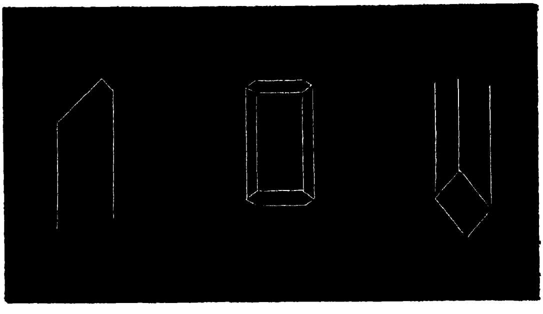
Analysis:—

0·1392 gram substance gave 0·0833 gram H_2O and 0·4023 gram CO_2.

	Theory. $C_{13}H_{13}NO$.	Found.
C	78·39 per cent.	78 82 per cent.
H	6·54 „	6·65 „

This substance is *phenyllutidone*.

Phenyllutidone melts at 196—197°. It is easily soluble in warm water and alcohol, less so in benzene. From the hot solution in water or benzene, it crystallises on cooling in colourless needles. This substance is identical with the phenyllutidone obtained by Conrad and Guthzeit (*Ber.*, 20, 161), by heating phenyllutidonedicarboxylic acid at 270°. The platinochloride is easily prepared by adding platinum chloride to the solution of phenyllutidone in hydrochloric acid. It is thus obtained as a yellow powder, which crystallises from water in yellow needles; these, when examined under the microscope, are found to have the following forms:—



Analysis:—

0·3017 gram substance gave 0·1080 gram H_2O, 0·4286 gram CO_2, and 0·0726 gram Pt.

	Theory. $(C_{13}H_{13}NO)_2,H_2PtCl_6$.	Found.
C	38·52 per cent.	38 68 per cent.
H	3·46 „	3 97 „
Pt	24·32 „	24·09 „

This platinochloride has also been prepared by Conrad and Guthzeit from their phenyllutidone from phenyllutidonedicarboxylic acid. Both salts were found to be identical, not only in appearance but also in behaviour.

I am at present engaged on further experiments on dehydracetic acid, the results of which I hope to be able to bring before the Society in a short time.

XLVIII.—*A Contribution to the Study of Well Waters.*

By Robert Warington, F.R.S.

During recent years determinations have been made of some of the more important constituents of the rain and drainage waters collected at Rothamsted; the results of these determinations have been in great part already published.* Still more recently a systematic examination has been made of some of the deep well waters of the same district. It is proposed in the present communication to bring together these results, and to trace the connection between the composition of rain, drainage, and deep well waters. It is hoped that in this way some light may be thrown on the natural history of well waters.

Rain Water.

The primary source of all drainage and well water is rain. The rain has been systematically collected at Rothamsted since 1853 in a large gauge having an area of 1–1000th of an acre. Details as to the quantity of rain collected, and respecting the investigations into its composition carried on at Rothamsted, and also by Professor Way, and by Dr. E. Frankland, will be found in the Rothamsted Reports already referred to. It will suffice for our present purpose to notice the average amount of some of the constituents of the rain water, as determined in the Rothamsted Laboratory.

---

* "The Amount and Composition of the Rain and Drainage Waters collected at Rothamsted, by Sir J. B. Lawes, Dr. J. H. Gilbert, and R. Warington" (*Jour. Roy. Agri. Soc.*, 1881, 241, 311; 1882, 1). Also "New Determinations of Ammonia, Chlorine, and Sulphuric Acid, in the Rain Water collected at Rothamsted, by Sir J. B. Lawes, Dr. J. H. Gilbert, and R. Warington" (*Jour. Roy. Agri. Soc.*, 1883, 313).

TABLE I.—*Chlorine, Sulphuric Anhydride, and Ammonia in Rain Water at Rothamsted, Herts.*

1. Chlorine, Average of Nine Years, 1877–86.

	Rainfall, inches.	Chlorine.	
		Per million of rain.	Pounds per acre.
January	2·24	3·35	1·70
February	2·61	2·65	1·56
March	1·40	3·48	1·10
April	2·45	1·77	0·98
May	2·48	1·43	0·80
June	2·72	1·15	0·71
July	2·70	0·82	0·50
August	3·01	1·06	0·72
September	3·00	1·22	0·83
October	3·86	2·73	2·04
November	3·30	2·68	2·00
December	2·38	2·71	1·46
April—September	16·36	1·23	4·54
October—March	15·29	2·85	9·86
Whole year	31·65	2·01	14·40

2. Sulphuric Anhydride, Average of Five Years, 1881–86.

	Rainfall, inches.	Sulphuric anhydride.	
		Per million of rain.	Pounds per acre.
April—September	14·16	2·67	8·57
October—March	16·06	2·39	8·69
Whole year	30·22	2·52	17·26

3. Ammonia, Average of Five Years, 1881–86.

	Rainfall, inches.	Nitrogen as ammonia.	
		Per million of rain.	Pounds per acre.
January	2·77	0·29	0·181
February	2·25	0·28	0·140
March	1·43	0·48	0·155
April	2·21	0·48	0·242
May	1·77	0·47	0·188
June	2·61	0·44	0·258
July	2·18	0·48	0·236
August	2·38	0·39	0·210
September	3·01	0·30	0·204
October	3·71	0·26	0·221
November	3·25	0·23	0·169
December	2·65	0·34	0·202
April—September	14·16	0·42	1·338
October—March	16·06	0·29	1·068
Whole year	30·22	0·35	2·406

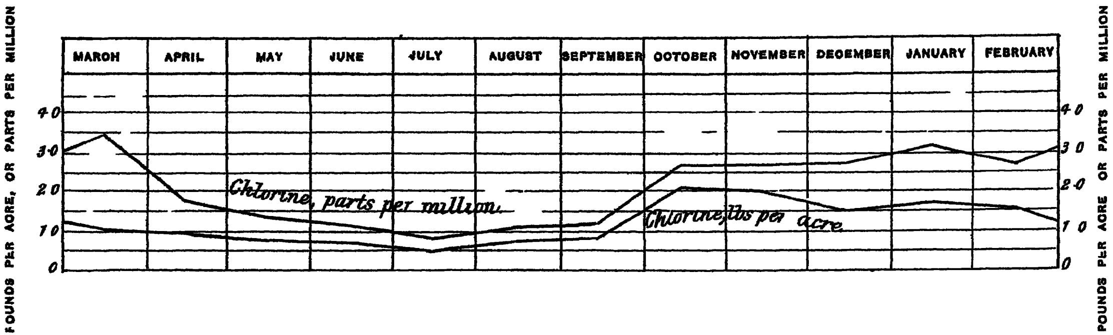
1. *Chlorine.*—The amount of chlorine present in the rain water at Rothamsted during each month of the year, on an average of nine years, is given in Table I; the same amounts are graphically depicted in the following Chart. The average proportion of chlorine is 2·01 per million of rain; this proportion, with a rainfall of 31·65 inches, amounts to 14·4 lbs. per acre in a year, which is equivalent to 24 lbs. of pure sodium chloride. The monthly averages of the amount of chlorine given in the table exhibit considerable variations at different seasons of the year. The amount of chlorine in the six winter months (October to March) is indeed rather more than twice as great as it is during the summer half of the year. There is a plainly marked minimum in July; the amount of chlorine rises pretty regularly on each side of this month.

At Cirencester the amount of the chlorine has been determined in half-yearly mixtures of the rain for 16 years (Trans., 1887, 92). Omitting one very abnormal half-year, the average proportion of chlorine is 3·25 per million, and the annual quantity 24·4 lbs. per acre, equivalent to 40·3 lbs. of sodium chloride. The average rainfall was 33·31 inches. The winter rain contained more chlorine than the summer rain, but the difference is not nearly so considerable as at Rothamsted. The much larger amount of chlorides found at Ciren-

Journ Chem Soc June 1887

To face page 502

AMOUNT OF CHLORINE IN THE MONTHLY RAINFALL AT ROTHAMSTED, AVERAGE OF 9 YEARS



VARINGTON —PLATE A

Harrison & Sons Lith St Martins Lane

cester than at Rothamsted is clearly due to the position of the former locality in the west of England, and to its being nearer the sea.

Many determinations of chlorine in rain water from various parts of the United Kingdom have been made by Dr. Angus Smith ("Air and Rain; the beginnings of a Chemical Climatology," 1872). More recently the chlorine in rain water collected in London has been determined by Dr. W. J. Russell (Appendix to "Monthly Weather Report," April, 1884). All these determinations refer, however, only to special samples of rain water, and do not supply data for calculating the average proportion of chlorine in the whole rainfall of the year. Dr. A. Smith gives 3·88 per million as the average proportion of chlorine in the rain water of inland country places in England; and 3·28 per million as the proportion for similar districts in Scotland. In towns, or near the sea, the proportion is considerably higher.

2. *Sulphuric Acid.*—The average proportion of sulphuric anhydride in the rain water at Rothamsted, during five years, has been 2 52 per million. This proportion, with a rainfall of 30·22 inches, amounts to 17·26 lbs. per acre per annum. The quantity in summer and winter is very similar.

Many determinations of sulphuric acid in particular samples of rain water have been made by Dr. Angus Smith, and by Dr. W. J. Russell.

3. *Ammonia.*—The determinations of ammonia in the monthly rainfall at Rothamsted give an average proportion of 0·35 of ammoniacal nitrogen per million of rain water, on an average of five years. This proportion amounts to 2·4 lbs. per acre in the year, with a rainfall of 30·22 inches. There is, on the average, a distinct excess of ammonia in the summer months, but the series is too short to exhibit any regular order throughout the year.

Determinations of ammonia in rain have also been made by Dr. Angus Smith, and Dr. W. J. Russell.

4. *Nitric Acid and Organic Nitrogen.*—The determinations of nitric acid in the Rothamsted rain made by Way and Frankland, showed the amount of nitrogen in this form in the annual rainfall to be about 1 lb. per acre. The nitrogen as organic matter found by Frankland amounted also to about 1 lb. per acre per annum. These amounts are approximate only, as in Frankland's analyses no complete year's rainfall was examined. New determinations of nitric acid are now in progress at Rothamsted.

The total combined nitrogen in the annual rainfall appears from the figures at command to be about 4·4 lbs. per acre, or (with a rainfall of 29 inches) 0·67 per million of rain.*

---

* I cannot conclude the above brief notice of the composition of rain water without calling attention to the excellent work on this subject carried out by Prof.

DRAINAGE WATERS.

Of the rain which falls upon a soil a considerable portion is evaporated, either from the surface of the soil, or through living vegetation. When the amount of rain exceeds the amount of water evaporated from the land, a portion of the rain water passes downwards through the soil, and appears as drainage water. The composition of this drainage water is the main factor which determines the composition of well waters. In the investigations at Rothamsted the composition of drainage waters both from uncropped and unmanured land, and also from land both cropped and manured has been ascertained.

Drainage Water from Uncropped and Unmanured Land.

The three drain-gauges at Rothamsted are fully described in the paper already cited. They consist of rectangular masses of soil, having an area of 1–1000th of an acre, and depths of 20, 40, and 60 inches. These masses of soil were part of an arable field; they were isolated without being disturbed. They are supported below by perforated iron plates, and are surrounded by walls of brick and cement. The water percolating through these soils is collected and analysed. The soil is in every case a heavy loam, mixed with flints, and having a clay subsoil; it has been unmanured since 1870, and has been kept free from vegetation.

1. *Amount of Drainage.*—The amounts of drainage from the three drain-gauges are very similar. As the drainage from the deepest soil (5 feet) will most nearly represent the supply passing downwards to the wells, we shall confine attention chiefly to this.

In Table II we have the average rainfall, and the average amount of drainage through 5 feet of soil during the last 16 years, 1871–86.

It appears from these figures, that with an average rainfall of 31·04 inches, there has been an annual evaporation of 17·09 inches from the surface of the bare soil, while an average of 13·95 inches has percolated to a depth exceeding 5 feet, and appeared as drainage. Evaporation is naturally most active during the summer months, and the amount of drainage is then at a minimum. With October the

---

G. Gray at Canterbury College, Lincoln, New Zealand, during 1884 and 1885. The average composition of the rainfall at Lincoln in these two years he found to be: Chlorine, 7·74; sulphuric anhydride, 2·01; ammoniacal nitrogen, 0·12; nitric nitrogen, 0·14; albuminoid nitrogen, 0·09; total dissolved matter, 28·6 per million. These numbers are the true averages, and are not the mean of the monthly determinations. The average rainfall was 25·29 inches It is interesting to note that, as in England, the chlorine is most abundant in the winter months, although the winter at Lincoln is actually at the time of our summer.

period of considerable drainage commences, and continues till the end of February. In these five winter months the average drainage has amounted to 9·44 inches, while in the remaining seven months of the year the drainage has been but 4·51 inches. It is by the autumn and winter drainage that the supply of water to the wells is chiefly effected.

The dependence of the proportion of drainage on the amount of evaporation is strikingly seen if we compare summer and winter months having a similar rainfall. Thus in August, with 2·50 inches of rainfall, 1·97 inch evaporates, and 0·53 inch appears as drainage; while in December, with 2·55 inches of rainfall, the proportions are reversed, only 0·61 inch[*] evaporates, and 1·94 inch appears as drainage.

The very variable distribution of rain throughout the year in different seasons, and the consequent irregular distribution of drainage, are illustrated by the characters of the individual seasons recorded in Table IV (p. 511). So irregular indeed has been the

TABLE II.—*The Average Monthly Rainfall, Evaporation, and Drainage through 5 feet of bare Soil.*

	Average of 16 years, 1871—1886.		Rainfall; average of 34 years, 1853-86.	Water evaporated, or retained by the soil; average of 16 years.	Water probably appearing as drainage with normal rain.
	Rainfall.	Drainage (actual).			
	inches.	inches.	inches.	inches.	inches.
March	1·58	0·66	1·67	0·92	0·75
April	2·32	0·75	2·04	1·57	0·47
May	2·21	0·54	2·30	1·67	0·63
June	2·56	0·54	2·44	2·02	0·42
July	2·88	0·61	2·62	2·27	0·35
August	2·50	0·53	2·56	1·97	0·59
September	2·98	0·88	2·66	2·10	0·56
October	3·39	1·71	3·21	1·68	1·53
November	3·13	2·09	2·49	1·04	1·45
December	2·55	1·94	2·23	0·52[†]	1·71
January	2·69	2·10	2·58	0·59	1·99
February	2·25	1·60	1·86	0·65	1·21
March—Sept.....	17·03	4·51	16·29	12·52	3·77
Oct.—Feb.	14·01	9·44	12·37	4·48	7·89
Whole year......	31·04	13·95	28 66	17·00	11·66

---

[*] The average of 15 years, 1871–85, is 0·52 inch. This will be nearer the truth than the average of 16 years, as in December, 1886, the snow falling in that month melted in the following, and thus disturbed the relation of rain to drainage.

[†] Average of 15 years, 1871–85.

distribution of rain, that the average results of the last 16 years do not quite accurately express the normal amounts of rain and drainage We shall obtain a more exact notion of the normal monthly drainage from a bare clay soil like that filling the drain-gauges, by taking the average monthly rainfall during 34 years, as determined at Rothamsted, and deducting from this the monthly evaporation from the soil shown in the 16 years' observations of the soil in the drain-gauge. This mode of calculation gives the distribution of drainage throughout the year with more correctness, in consequence of the greater constancy of evaporation than rainfall. The results of this calculation are shown in Table II; they will be found graphically depicted in the Chart opposite p. 514.

Before leaving this part of the subject it must be noticed that the proportion of rain appearing as drainage in the Rothamsted drain-gauges has undergone a distinct increase during the later years of the experiment, a result possibly due to some alteration in the physical conditions of the soil.

2. *Composition of Drainage Water.*—In Table III we have the average monthly amount of chlorine and nitric nitrogen in the drainage waters from the shallowest and deepest of the drain-gauges; the figures given are the average of nine years, June, 1877, to May, 1886.

The drain-gauges having been constructed in the autumn of 1870, the soils they contain had undergone washing by rain for seven years before the exact sampling of the drainage water commenced. Some analyses of the earlier drainage waters will be found in the paper on Rain and Drainage already referred to. The proportion both of chlorides and nitrates was decidedly greater in the earlier samples than it is at present.

The total quantity of chlorine in the yearly drainage from the soils of the drain-gauges is seen to be practically identical with that present in the annual rainfall. The chlorine in the drainage waters from the two drain-gauges averages 14·63 lbs. and 14·05 lbs. per acre; while that in the rainfall during the same period is 14·40 lbs. It is evident, therefore, that any chlorides originally belonging to the soils of the drain-gauges have been thoroughly washed out, and the quantity now present is entirely due to the amount supplied by the rain. Though the total quantity of chlorine in the drainage waters is identical with that in the rain, the proportion of chlorine per million of water is nearly doubled; that in the rain being 2·01, and that in the drainage water 3·9 per million. This increase in the proportion of chlorine is a natural consequence of the evaporation that has taken place from the soil; nearly one-half of the rainfall has evaporated from the bare uncropped soil, and the proportion of chlorine found in the drainage water is thus almost double that in the rain.

TABLE 'ne, nd *Nitrogen as* 'es, *in the Drainage Water* m un *inured bare S* 20 *and* 60
deep, at Rothan *Average of Nine Years, Ju* 1877 *May*, 1886.

	Rain-fall.	Amount of drainage.		Chlorine.				Nitrogen as nitrates.				Nitrogen to 100 chlorine.	
				Per million of water.		Per acre.		Per million of water.		Per acre.			
		20-in. gauge.	60-in. gauge.	20-in. gauge.	60-in. gauge.	20-in. gauge.	60-in. gauge.	20-in. gauge.	60-in. gauge.	2)-in. gauge.	60-in. gauge.	20-in. gauge.	60-in. gauge.
	ins.	ins.	ins.			lbs.	lbs.			lbs.	lbs.		
March	1·40	0·57	0·61	4·0	4·0	0·52	0·55	6·2	8·9	0·80	1·22	153	223
April........	2·45	0·90	0·98	3·9	3·6	0·80	0·80	8·2	9·0	1·67	2·00	210	250
May	2·48	0·79	0·79	4·2	4·0	0·75	0·71	8·8	9·9	1·57	1·78	210	249
June	2·72	0·75	0·74	3·6	3·6	0·61	0·61	9·4	9·8	1·59	1·65	260	269
July	2·70	0·61	0·54	4·4	4·3	0·61	0·52	15·5	13·2	2·12	1·62	350	311
August	3·01	1·04	0·93	3·3	3·7	0·77	0 77	15·9	13·9	3·73	2·92	483	381
September ...	3 00	1·26	1·09	3·8	3·8	1·09	0·93	17·6	13·5	5·02	3·32	461	355
October......	3·36	2·13	1·95	3·8	3·9	1·85	1·73	13·2	11·7	6·35	5·17	344	299
November....	3·30	2·46	2·32	3·9	4·1	2·18	2·17	10·8	11·0	6·00	5·78	275	266
December....	2·38	2·00	1·99	3·9	3·9	1·76	1·74	9·1	10·7	4·11	4·80	234	277
January	2·24	1·91	1·94	3·7	3·8	1·58	1·65	7·6	9·3	3·31	4·10	209	248
February.....	2·61	2·35	2·17	4·0	3·8	2·11	1·87	7·4	9·0	3 96	4·41	188	236
March—June.	9·05	3·01	3·12	3·9	3·8	2·68	2·67	8·3	9·4	5·63	6·65	210	249
July—Sept. ..	8·71	2·91	2·56	3·8	3·8	2·47	2·22	16·5	13·6	10·87	7·86	440	354
Oct.—Feb. ..	13·89	10·85	10·37	3·9	3·9	9·48	9·16	9 7	10 3	23·73	24·26	250	265
Whole year ..	31·65	16·77	16·05	3·9	3·9	14·63	14·05	10·6	10·7	40·23	38·77	275	276

The distribution of the chlorine throughout the year is apparently almost entirely governed by the amount of the drainage, the proportion of chlorine per million of water, saving a rather high figure for July, being fairly uniform in every month. The well marked winter maximum of chlorine in the rain water is in fact neutralised by the smallness of the evaporation at this period of the year; while the small proportion of chlorine supplied by the rain in summer is magnified by the large evaporation from the soil which then takes place.

The amount of chlorine in the drainage water we have just seen to be identical with that furnished by the rain; when we turn to the nitrogen occurring in the drainage water the case is very different. The total quantity of combined nitrogen in the annual rainfall we have seen to be about 4·4 lbs. per acre. The nitrogen in the form of nitrates in the drainage waters from the two unmanured and uncropped soils amounts to 40·23 lbs. and 38·77 lbs. per acre. The drainage waters contain mere traces of ammonia. A small quantity of organic nitrogen, equal to about 2 lbs. per acre per annum, is shown by Frankland's analyses of early samples of these waters. The total amount of combined nitrogen in the drainage waters is thus about 40—42 lbs. per acre per annum.

The large production of nitrates in the soils of the drain-gauges is due, as is now well known, to the oxidation of the nitrogenous organic matter of the soil, brought about through the action of a bacterium. This nitrogenous organic matter of soil consists chiefly of the accumulated residues of previous vegetation. Determinations of nitrogen in the soils forming the drain-gauges showed the presence of 3500 lbs. of nitrogen per acre in the first 9 inches, and about 13,000 lbs. to the depth of 60 inches.

The subject of nitrification has been already on several occasions brought before the Chemical Society (Trans., 1878, 44; 1879, 429; 1884, 637; 1885, 758; 1887, 118). Numerous investigations have also been made at Rothamsted on the amount of nitric acid occurring in agricultural soils of known history (*Chem. Soc. J.*, Trans., 1882, 351; *Jour. Roy. Agri. Soc.*, 1883, 331; *Chem. Soc. J.*, Trans., 1885, 380). We need only on the present occasion refer to those facts concerning the process of nitrification in soil which directly influence the composition of the drainage and well waters we are considering.

The average monthly composition of the drainage waters given in Table III, shows that nitrification proceeds in the soil with very different energy at different periods of the year. Looking first at the drainage from the shallowest soil (the 20-inch drain-gauge), we see that the minimum contents of nitrates, 6·2 of nitrogen per million, occurs in March; from this point the amount slowly rises to 9·4 per million in June. A great leap to 15·5 per million occurs in July, and the maximum for the year, 17·6 per million, is reached in September. After this month the proportion of nitric acid gradually declines, till the minimum is again reached in March. These proportions of nitric nitrogen in the drainage water represent the *average* of nine years' results; in individual seasons, the periods of maximum and minimum, and their relative values, are more or less varied. It may be taken, however, as a rule, that in every season the maximum proportion of nitrates in the drainage water occurs in the first month after July in which a considerable amount of drainage takes place.

The cause of the regular alteration in the proportion of nitrates in the drainage waters at different seasons of the year is clearly due to the influence of temperature on the process of nitrification. Summer is the season in which nitrification chiefly occurs in the soil; the nitrates of the autumn and winter drainage largely consist of nitrates formed in the soil during the summer, which are washed out when the period of active drainage sets in. The time of year when the minimum strength of the drainage water occurs, and the proportion of nitrates at this period, will depend very much on the amount of washing which the soil undergoes.

Some notable differences occur between the composition of the drainage water from 20 inches and 60 inches of soil. The greater depth, and therefore bulk, of the latter soil, equalises to a remarkable extent the strength of the drainage water. With the 20-inch drain-gauge, we have an average variation in strength from 6·2 to 17·6 of nitric nitrogen per million of drainage water in different months of the year; with the 60-inch drain-gauge, the variation is only from 8·9 to 13·9. We may thus safely infer that at a greater depth the composition of the drainage water would be uniform throughout the year; this would at least be the case if the drainage occurred entirely through the mass of the soil, and no water came directly from the surface through open channels. At different times of the year drainage coming directly from the surface will be much stronger, or much weaker, than the general discharge from the saturated soil.* The general presence of fissures and channels in the soil must be always taken into account when studying the phenomena of polluted wells.

The quantity of nitrates which passes away in the drainage waters is naturally governed in great measure by the quantity of the drainage. We have already seen that the principal amount of drainage occurs between October and February. The period of most active drainage thus commences soon after the soil has attained its maximum contents in nitrates; a double maximum of intensity and quantity thus generally occurs in the autumn months, and the discharge of nitrates at this season is in consequence very considerable. In the case of the shallowest soil (20 inches), October is, on an average, the month in which the greatest discharge of nitrates takes place. With the deepest soil (60 inches), the maximum discharge is in November; the greater bulk of soil inducing a longer retention of the nitrates. In the five months, October to February, 62 6 per cent. of the whole annual discharge of nitrates appear on an average in the drainage from the deepest soil; while in the remaining seven months only 37·4 per cent. appear. The average monthly proportion of nitrates in the drainage waters from the shallowest and deepest drain-gauges, with the actual quantities of nitric nitrogen discharged, are graphically depicted in the accompanying Chart.

---

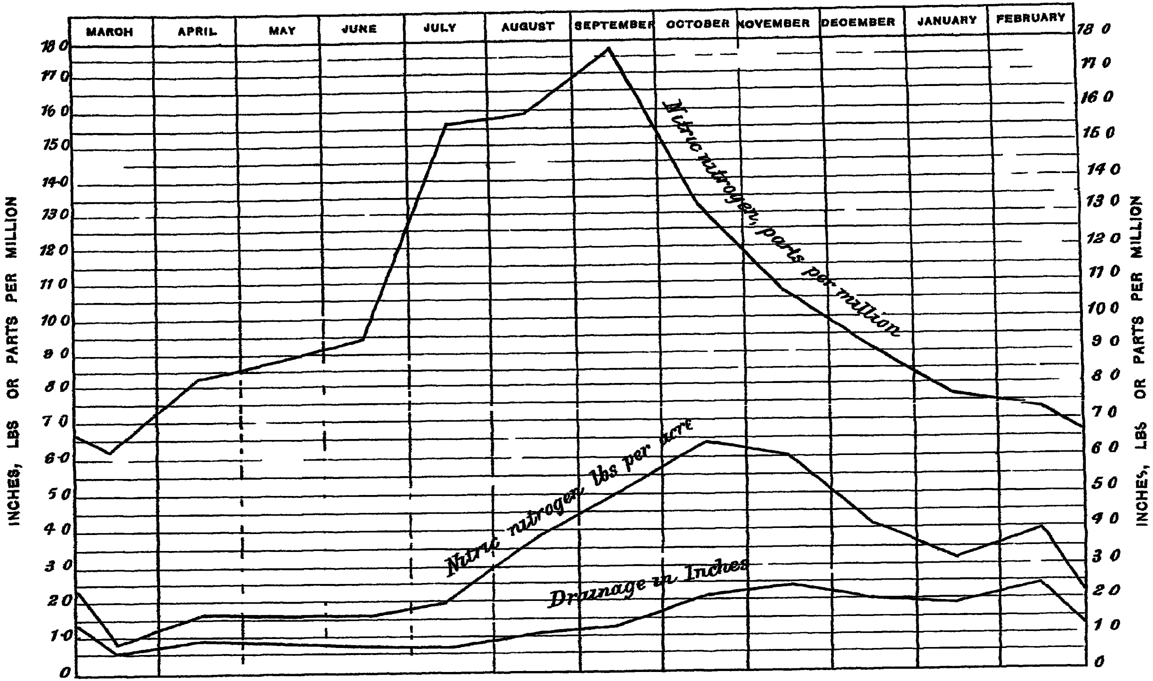
* The difference in composition, under varying conditions, of water derived from the general drainage of the soil, and of that coming directly from the surface, is discussed, with numerous illustrations from the Rothamsted experiments, in the paper on Rain and Drainage already referred to.

In Table IV will be found the quantity of drainage through the 60-inch drain-gauge, and its contents in nitrates, during the years 1877–86; this will furnish ample illustration of the characters and variations of individual seasons, during some of which the alterations in composition taking place in deep well waters were also studied.

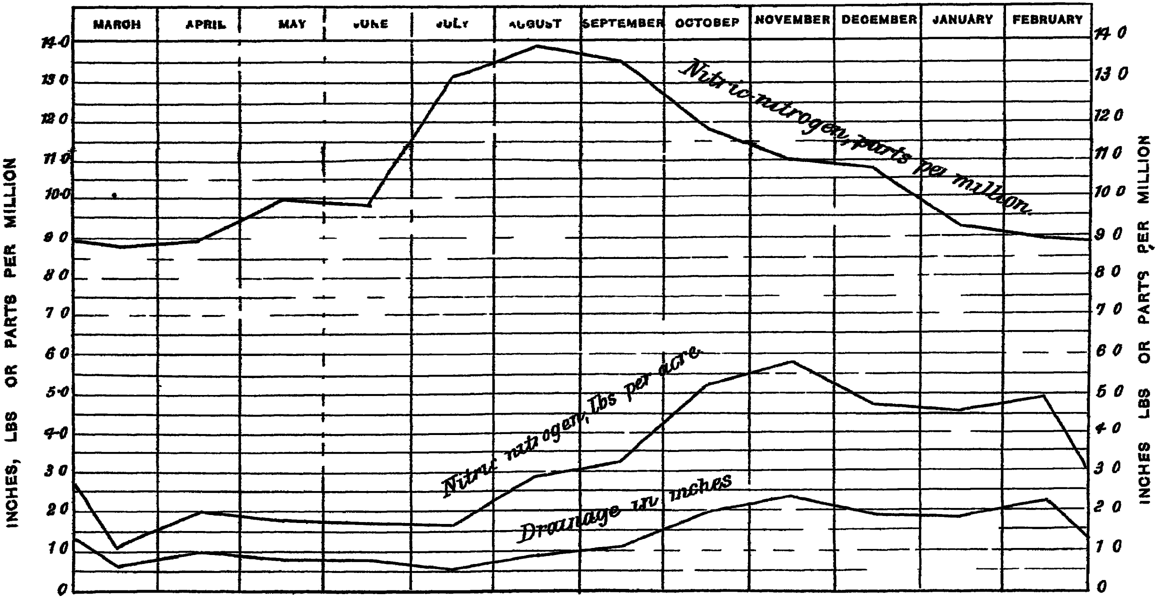
3. *General Conclusions.*—The general bearing of the facts now mentioned upon the character of the drainage waters which furnish the supply to wells may be briefly summarised as follows:—If the land forming the surface of a large drainage area was without vegetation, and unmanured, and the soil similar to the Rothamsted loam; if, moreover, the rainfall was similar in quantity and composition to that of Rothamsted, then the water passing downwards to form deep well water would contain about 4 per million of chlorine, and 10 to 11 per million of nitrogen as nitric acid. The quantity of water in the wells would vary, the maximum depth of water occurring at some later date than the period (October to February) of maximum drainage from the surface. The composition of the water would, however, remain constant throughout the year, excepting the percolation took place in part through open channels communicating directly with the upper soil. With soils more or less nitrogenous than that at Rothamsted, the proportion of nitric acid in the well water would vary; but the proportion of chlorine would be constant, unless the composition of the rain water, or its degree of concentration by evaporation from the soil, were affected.

AMOUNT OF DRAINAGE, AND OF NITROGEN AS NITRATES IN THE DRAINAGE WATER, FROM DRAIN-GAUGES CONTAINING BARE SOIL, AT ROTHAMSTED; AVERAGE OF 9 YEARS

BARE SOIL 20 INCHES DEEP



BARE SOIL 60 INCHES DEEP



WARINGTON—PLATE B

TABLE IV.—*The Amount of Monthly Drainage through 5 feet of Bare Unmanured Soil, and the Quantity of Nitrogen as Nitrates in the Drainage Water in pounds per acre.*

	1876–77.	1877–78.		1878–79.		1879–80.		1880–81.		1881–82.	
	Drainage	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.
	ins.	ins.	lbs.	ins.	lbs.	ins.	lbs.	ins.	lbs.	ins.	lbs.
March	1·59	1·11	—	0·46	1·54	0·26	0·82	0·09	0·25	1·65	2·47
April	1·72	1·49	—	3·47	5·96	1·33	3·48	0·43	1·39	0·03	0·08
May	0·03	0·51	1·75	1·50	4·76	1·30	2·91	0·03	0·10	0·04	0·09
June	0·00	0·10	0·33	0·76	2·36	2·19	4·60	0·02	0·08	0·04	0·05
July	0·00	0·44	1·95	0·06	0·19	1·81	4·66	1·06	3·84	0·01	0·02
August	0·03	0·31	1·54	1·13	4·32	4·35	11·21	0·22	0·79	2·21	8·15
September	2·04	0·21	0·98	0·11	0·42	0·92	2·77	3·78	10·69	0·70	2·28
October	0·96	0·39	2·06	1·10	4·14	0·43	1·27	4·07	9·95	1·53	4·68
November	2·66	3·82	10·90	3·67	9·54	0·10	0·30	2·14	5·28	2·29	6·12
December	5·25	1·75	5·67	1·54	4·12	0·44	1·21	2·68	5·70	3·65	8·17
January	4·11	1·20	4·13	2·47	6·26	0·46	1·47	1·32	1·97	1·23	2·91
February	1·23	1·13	3·00	4·22	8·78	2·30	6·72	3·29	5·50	1·01	2·43
March—September	5·41	4·17	—	6·45	19·55	12·22	30·45	5·63	17·14	4·68	13·14
October—February	14·21	8·29	25·81	13·00	32·84	3·73	10·97	13·50	28·40	9·71	24·31
Whole year	19·62	12·46	—	19·45	52·39	15·95	41·42	19·13	45·54	14·39	37·45

TABLE IV—(*continued*).

	1882–83.		1883–84		1884–85.		1885–86.		1886–87.	
	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.	Drainage.	Nitric nitrogen.
	ins.	lbs.	ins.	lbs.	ins.	lbs.	ins.	lbs.	ins.	lbs
March............	0·49	1·18	0·09	0·17	1·10	2·12	0·67	1·28	0·69	1·16
April............	1·57	3·38	0·22	0·41	0·19	0·44	0·93	1·74	0·58	1·08
May	0·74	1·48	0·62	1·12	0·11	0·21	0·87	1·76	1·93	3·59
June	0·99	2·28	0·09	0·16	1·04	2·62	1·46	2·34	0·10	0·19
July	0·10	0·27	1·25	3·31	0·10	0·28	0·04	0·08	0·11	0·24
August	0·02	0·06	0·05	0·11	0·05	0·10	0·00	0·00	0·03	0·09
September	0·40	1·26	1·32	3·72	1·11	3·95	1·25	3·81	0·01	0·02
October..........	5·10	11·42	1·38	3·72	0·41	1·42	3·15	7·90	1·74	5·74
November	2·41	5·19	2·47	5·98	0·62	2·09	3·31	6·59	2·43	6·59
December.........	2·98	5·54	0·95	2·21	3·01	8·71	0·91	1·90	2·37	4·98
January	2·81	4·72	1·65	3·54	2·43	5·22	3·92	6·65	3·78	4·70
February..........	3·70	4·85	0·86	1·95	2·45	5·27	0·60	1·16	0·51	1·02
March—September .	4·31	9·91	3·64	9·00	3·70	9·72	5·22	11·01	3·45	6·37
October—February.	17·00	31·72	7·31	17·40	8·92	22·71	11·89	24·20	10·83	23·03
Whole year........	21·31	41·63	10·95	26·40	12·62	32·43	17·11	35·21	14·28	29·40

Drainage Water from Cropped Land.

By far the larger portion of the land forming drainage areas is covered either continuously, or at certain seasons of the year, by some natural or artificial vegetation.

1. *Amount of Drainage.*—The first influence of vegetation upon drainage which we have to notice is that it greatly diminishes the proportion of rain percolating through the soil, by increasing the amount of evaporation from the surface. The increase in the amount of evaporation is principally confined to the growing period of vegetation, and is determined by the transpiration of water through the plant. The more vigorous is the growth of a plant, the larger will be the quantity of water which it transpires. We have seen, from the results of the drain-gauges, that with an uncropped soil only a small proportion of the total drainage occurs, on an average, in the summer months. In the case of a soil bearing a vigorous crop, drainage is, in our climate, entirely suspended during summer, excepting the rainfall is unusually heavy and continuous. The turfed drain-gauges of Mr. J. Evans, and of Mr. Greaves, show hardly any percolation during the summer months. In the former drain-gauge, on an average of 15 years, 1860–1 to 1874–5, with a rainfall of 25·55 inches, the total drainage in the six months, April to September, amounted to 0·35 inch, or 6·3 per cent.; while the winter drainage was 5·23 inches, or 93·7 per cent. of the whole. In Mr. Greaves' turfed drain-gauge, on an average of 14 years, 1860–73, with a rainfall of 25·72 inches, the drainage during the summer six months was 0·73 inch, or 9·7 per cent.; and in the winter six months 6·85 inches, or 90·3 per cent.

A further illustration of the distribution of the drainage from cropped land throughout the year is afforded by the number of runnings of the drain-pipes in Broadbalk field at Rothamsted. This field has grown wheat continuously since 1843–4. Each plot is provided with a drain-pipe, 2—3 feet below the surface. The ends of these drain-pipes are uncovered, their runnings are recorded, and during the last eight years the drainage waters have been systematically analysed. The total daily runnings of the drain-pipes of two plots in each month during 20 years, 1867–86, are given in Table V. One of these plots is permanently unmanured, the other receives a complete manuring. The spring, summer, and early autumn runnings of the drain-pipes are fewest on the plot which bears the highest crop, and therefore evaporates the largest quantity of water.

A further result of the greater evaporation from a cropped soil during summer, is that the winter drainage commences at a later period. From the uncropped soil of the Rothamsted drain-gauges

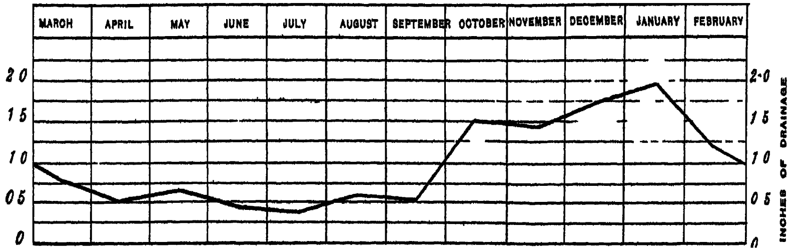
TABLE V.—*The Average Produce of Two Plots in Broadbalk Wheat Field, with the Total Daily Runnings of the Drain-pipes of these Plots during* 20 *Years*, 1867–86.

	Plots 3 and 4, unmanured.	Plot 7, manured.
Total produce per acre. Average of 20 years.	1713 lbs.	5315 lbs.
Runnings of drain-pipes—		
March	18	14
April	17	15
May	14	11
June	14	8
July	9	5
August	6	6
September	8	5
October	35	26
November	59	53
December	60	64
January	61	66
February	42	45
March—September	86	64
October—February	257	254
Whole year	343	318

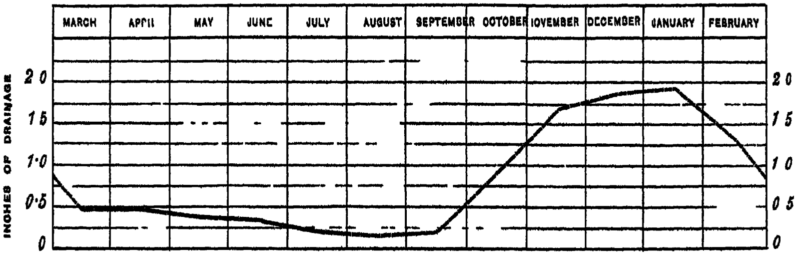
there is, on an average, a large drainage in October, the amount is maintained in November, and further increases in December and January, the last-named month yielding the maximum for the year (Table II, last column, p. 505). The turfed drain-gauge of Mr. Greaves, at Lee Bridge, shows a considerable increase of drainage in October; but the maximum comes much later, the drainage of October being to that of January as about 1 : 4; while with the uncropped soil at Rothamsted, the relative proportion of the drainage of the same months (assuming a normal rainfall) is about 3 : 4. In the case of fallow land we have already seen that the period of active drainage is five months, October to February. In the case of pasture, or of land carrying an autumn crop, it will be more accurately four months, November to February. Land carrying cereals, or other summer crop, will have a drainage lying between these extremes. The curves of the drainage from the cropped and uncropped drain-gauges are given on the opposite page, and also a curve representing approximately the drainage of the wheat land (mean of the two plots mentioned in Table V); this latter is intermediate in character between that repre-

AVERAGE MONTHLY DRAINAGE THROUGH UNCROPPED AND CROPPED SOILS.

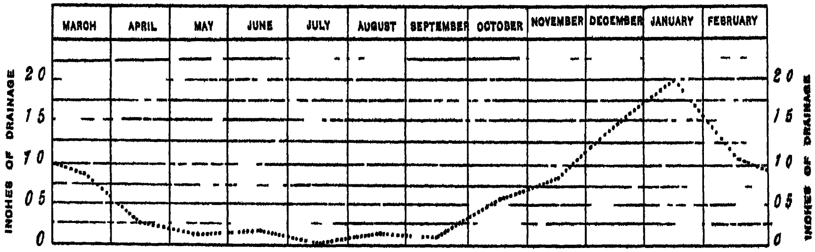
CALCULATED NORMAL DRAINAGE THROUGH 5 FEET OF BARE SOIL AT ROTHAMSTED



APPROXIMATE DRAINAGE THROUGH 2½ FEET OF WHEAT LAND AT ROTHAMSTED



DRAINAGE THROUGH 3 FEET OF TURFED SOIL AT LEE BRIDGE



WARINGTON—PLATE C

Harrison & Sons Lith St Martins Lane WC

senting the drainage of bare soil, and that representing the drainage from Mr. Greaves' turfed soil. The summer drainage shown by the runnings of the drain-pipes in the wheat field is somewhat above the truth, a running of a drain-pipe in summer implying less water than a running in winter. In comparing the three curves it must be recollected that the rainfall at Lee Bridge is somewhat smaller than that at Rothamsted.

2. *Composition of the Drainage from Wheat Land.*—We turn next to the influence of vegetation on the composition of the drainage water.

As the presence of vegetation greatly increases the amount of evaporation from the land, it would determine a greater degree of concentration in the drainage water, if none of the constituents dissolved in the water were removed by the growing vegetation. Both of the constituents, however, to which our attention is at present directed—the chlorides and the nitrates—are freely taken up by plants. The absorption of the first is to some extent limited; for, as it is not deposited in the plant tissues, the proportion of chlorides in the sap soon becomes greater than in the solution surrounding the roots, and then, as far as the operation of diffusion is concerned, the tendency will rather be for chlorides to leave the plant than to enter it. In the case of the nitrates, however, there is a rapid assimilation of the nitrogen after the entrance of the nitrates into the plant, and while this action continues the absorption of nitrates through the roots proceeds without check.

The analysis of the waters delivered by the drain-pipes underlying the plots of the experimental wheat field at Rothamsted affords information as to the composition of the water percolating through the soil at different times of the year. A detailed history of the field, and the composition of the drainage waters from the various plots, will be found described in the paper on Rain and Drainage, already mentioned. We shall consider, for our present purpose, first, the composition of the drainage water from the permanently unmanured wheat land; and secondly, the composition of the drainage from wheat land annually receiving farmyard manure. The composition of these drainage waters will be found in Table VI. The results are graphically represented in the Chart opposite p. 518.

Looking first at the average composition of the drainage water from the unmanured wheat land, we see that during eight years the average proportion of chlorine has been 6 per million. We have already seen (Table III) that during the last nine years the average proportion of chlorine in the drainage from an unmanured bare soil, has been 3·9 per million, while the proportion of chlorine in the rain (Table I) was 2 per million. If, therefore, we disregard the small

TABLE VI.—*Chlorine, and Nitrogen as Nitrates, in the Drainage Water from Wheat Land at Rothamsted.*

1. Unmanured 42 years. Average of Eight Years, 1878–86.

	Runnings of drain-pipes. (Days.)	Per million of water.		Nitrogen to 100 chlorine.
		Nitrogen as nitrates.	Chlorine.	
March	7	2·0	4·5	43·5
April	10	1·9	4·3	
May	6	0·8	3·3	12·7
June	8	0·1	2·9	
July	4	0·0	1·7	5·2
August	6	0·2	2·4	
September	5	3·9	9·0	50·8
October	20	4·9	9·3	
November	25	3·2	6·7	61·1
December	26	5·0	6·8	
January	14	3·2	4·8	67·3
February	34	4·1	6·1	
March—May	23	1·6	4·1	39·3
June—August	18	0·1	2·4	4·5
September—November	50	4·0	8·0	49·8
December—February	74	4·3	6·1	69·6
Whole year	165	3·4	6·0	55·8

2. Manured annually with 14 tons Farmyard Manure 42 years. Average of Eight Years, 1878–86.

March	1	4·5	4·1	90·8
April	1	3·4	4·6	
May	2	1·8	2·3	145·4
June	4	1·5	0·5	
July	0	—	—	—
August	1	0·1	0·2	50·0
September	2	6·1	9·2	67·8
October	6	7·7	11·2	
November	7	9·2	10·3	93·8
December	7	5·6	5·7	
January	10	5·2	7·7	80·0
February	9	7·8	8·4	
March—May	4	2·9	3·3	87·1
June—August	5	1·2	0·4	263·6
September—November	15	8·2	10·5	77·9
December—February	26	5·8	7·4	78·5
Whole year	50	5·8	7·3	79·7

3. Manured with Chloride and Sulphate of Ammonium in October, 1880.

October	3	14·9	96·7	15·4
November	4	41·8	49·0	91·4
December	3	21·7	23·2	93·5
February	3	22·9	19·4	118·0

amount of chlorine removed from the soil in the wheat crop,* we should conclude that, in round numbers, the rain had been concentrated to half its volume by the evaporation from the bare soil, and to one-third its volume by the evaporation from the cropped soil. This conclusion will be, at all events, very near the truth.

While the chlorine in the drainage has thus increased under the influence of a crop, the nitrates have considerably diminished. The drainage water from the uncropped land contained an average of 10·7 per million of nitrogen as nitrates; in the drainage water from the unmanured wheat land the average is only 3·4 per million.

In Table VI the attempt is made to exhibit the average composition of the drainage water from the wheat land during every month in the year. The number of analyses is at present insufficient to yield a smooth series of figures, but the general order of change throughout the year is plainly indicated. The irregularities are chiefly due to the fact that the composition of the drainage in any month varies much, according to the amount of washing the soil has already received. Thus the first running of drainage water after the cessation of drainage during the summer is always the richest in chlorides, and frequently the richest in nitrates; but this first running may occur in any month from September to February. It is obvious, therefore, that the *normal* progress of change between September and February can only be ascertained from the average of many years' analyses. In the graphic representation which follows, the autumn portion of the curve has been smoothed by plotting the mean composition of November and December between those two months, and proceeding in the same way with January and February. The composition of the drainage waters during the middle summer months is probably too low, at least as far as the chlorides are concerned, as the figures for those months are largely obtained from runnings occurring in 1879, a year of excessive and persistent rainfall, when the soil was to a great extent washed out.

The general course of change in the composition of the drainage waters throughout the year is, notwithstanding the irregularities, very evident. As spring advances the proportion of nitrates in the waters rapidly diminishes, instead of increasing as in the case of the drainage from uncropped soil. When the spring is a very forward one, as in 1884, the nitrates may have disappeared from the drainage waters of the unmanured plot as early as March. In other years the disappearance takes place in April or May. In June it is rare to find nitrates in this drainage water. Out of the 18 samples of drainage collected in June, July, and August, only two contained any nitric acid. In September, the crop having been removed, the waters are sure to contain nitrates. The proportion of nitrates in the drainage now rapidly increases. In a wet season the maximum will occur in October. In a normal season the proportion of nitrates after October will diminish very gradually till March; the disappearance then becomes more rapid, the new wheat crop commencing to assimilate the food at its disposal.

---

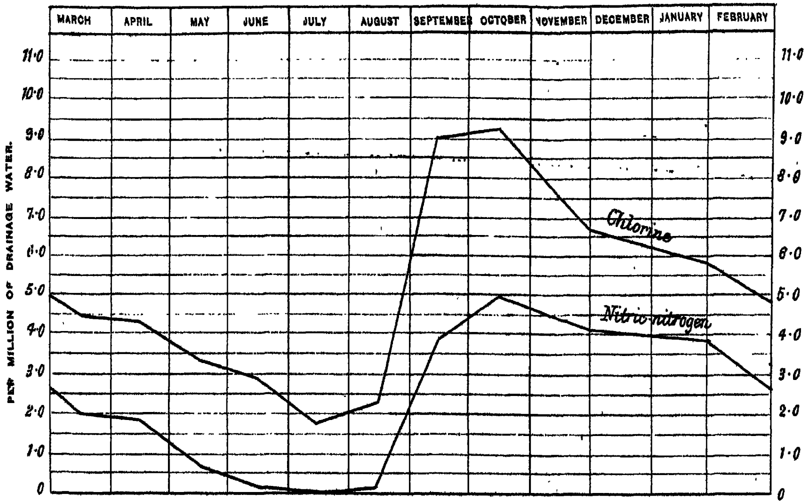
* The amount of chlorine in the ash of the unmanured wheat crop, during the eight years in question, would average less than 1 lb. per acre.

While the nitrates are going through this cycle of change, the chlorides are passing through a somewhat similar cycle. The chlorides in the drainage water are, however, only diminished, they are never wholly removed; the proportion of nitrates to chlorides in the drainage water suffers in consequence a great diminution as summer advances, the former being assimilated to a greater extent than the latter. After harvest there is a wonderful rise in the amount of chlorides in the drainage water. It is difficult to explain this without assuming that a large part of the chlorides removed by the wheat plant from the soil has been returned to the soil during the withering of the stem and leaves. As there is no process corresponding to nitrification by which chlorides are produced in the soil, the proportion of chlorides in the drainage water diminishes during the washing of the soil in the winter months far more rapidly than the proportion of nitrates; the maximum ratio of nitrates to chlorides is usually reached in February.

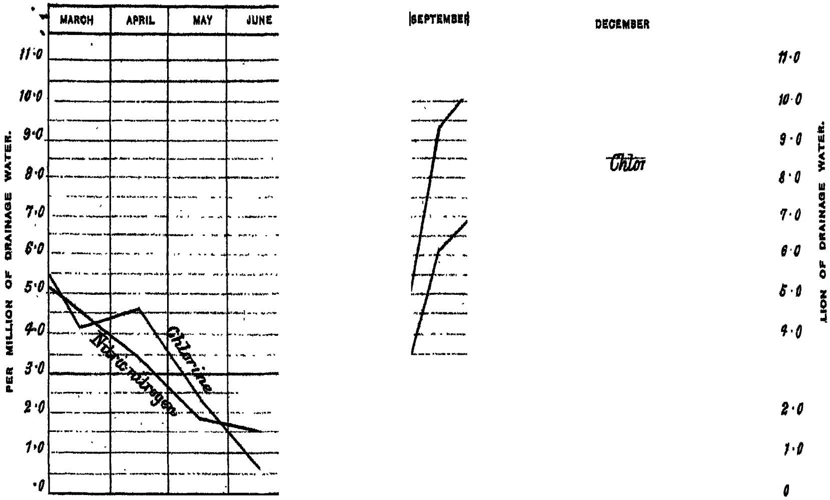
The number of analyses of drainage water from the plot manured each year (in October) with farmyard manure, is much fewer than that of the analyses of drainage water from the unmanured plot, the drain-pipe from the farmyard manure plot running very seldom; the monthly averages given in the table are consequently more irregular, and less to be depended on. The cycle of change throughout the year is evidently, however, quite similar to that presented by the water from the unmanured plot, but the proportion both of nitrates and chlorides in the water is larger. The average amount of chlorine per million of water is 7·3. The average proportion of nitric nitrogen is 5·8 per million. The proportion of nitrogen to chlorine is thus higher in the drainage from the manured than in that from the unmanured plot.

CHLORINE, AND NITROGEN AS NITRATES, IN THE DRAINAGE WATER FROM WHEAT LAND AT ROTHAMSTED, AVERAGE OF 8 YEARS.

WHEAT LAND WITHOUT MANURE.



WHEAT LAND RECEIVING FARMYARD MANURE EACH YEAR



WARINGTON.—PLATE D.

Harrison & Sons, Lith. St Martins Lane W.C.

The amount of farmyard manure at a farmer's disposal is so limited —about 1—2 tons per acre per annum—that its effect on the composition of the drainage water of any district must be very small, and almost negligible.

3. *General Conclusions.*—The information furnished by the drainage waters from the wheat field at Rothamsted enables us to form some idea of the composition of the water passing downwards from land under cereal culture. With rainfall, soil, and crop like those during the eight years at Rothamsted, the drainage from unmanured wheat land would contain 6 per million of chlorine, and 3·4 per million of nitric nitrogen. These are, however, minimum figures, which would be exceeded in average seasons, and on average land. The eight seasons in question were in fact seasons of excessive rainfall. If we might assume that the strength of the drainage water would vary inversely with the amount of drainage, then the drainage from the unmanured plot in the wheat field would in normal seasons contain about 8 per million of chlorine, and 4·5 per million of nitrogen as nitrates.* This proportion of nitrates would be probably still below an average, for we have further to remember that the soil of the unmanured wheat plot has been impoverished by the growth of about 40 crops without manure; the soil is thus below the general condition of soil in England, the crop being in fact less than one-half of an average wheat crop in this country. With average soils, richer in nitrogen, the proportion of nitrates in the drainage water would be increased.

In parts of England where the proportion of chlorides in the rain is greater than at Rothamsted, the proportion of chlorine in the drainage water would of course be increased. Thus at Cirencester, with an average of 3·25 parts of chlorine per million of rain, we should get, with an evaporation of two-thirds, a drainage water containing 9·75 parts of chlorine per million of water.

Land growing cereals will represent about half the land in arable culture in this country. Of the composition of the drainage from land growing fodder or root crops, or from land in permanent pasture, or covered with timber, we have, unfortunately, no direct evidence. The average amount of nitrates in the drainage water should be less from land carrying fodder or root crops in the autumn months than from land growing cereals, and still less in the case of land forming permanent pasture.

---

* The earlier analyses of these drainage waters, made by Dr. Voelcker and Dr. Frankland, show a higher proportion of nitrates, and a much higher proportion of chlorides than the later series of analyses given above. The mean of 16 analyses of the drainage from the unmanured plot gave nitrogen as nitrates 5·7, and chlorine 12·8 per million; while 10 analyses of the drainage from the farmward manure plot gave a mean of 8·9 of nitric nitrogen, and 15·6 of chlorine per million of water. The seasons in which these drainage waters were collected (December, 1866—February, 1873) were exceptionally dry. The mode of collecting the drainage waters was also not so perfect as at present, there being then more risk of contamination from other manured plots; this is explained in the paper on Rain and Drainage already referred to. The figures yielded by these analyses are thus certainly above the average for the drainage waters in question.

The influence of green crops upon the proportion of chlorine in the drainage is not so plain. By producing more evaporation from the soil they would tend to increase the proportion of chlorides in the drainage; on the other hand, much larger quantities of chlorides would be taken up by green crops than by cereals; but if these crops are finally consumed on the farm, and the manure brought back on to the fields, the only actual loss would be the quantity contained in the meat and milk sold in the towns.

In practical agriculture, the application of chlorides to the land in the form of purchased manure, as common salt, kainite, and guano, is very small, and probably quite negligible. Common salt is characteristic of human diet, and finds its way into the sewage channels.

The evidence afforded by the composition of the unpolluted well and spring water from permeable strata throughout England, which we shall bye-and-by have to notice, clearly shows that the average proportion of nitric nitrogen in the water percolating through the soil is usually 3—4½ per million. While the evidence of wells about Rothamsted clearly shows that in this district the average proportion of chlorine in land drainage cannot at most exceed 11 per million, and is probably less.

THE WELL WATERS OF HARPENDEN.

The well waters of which I have to speak occur in or near the village of Harpenden, and within a short distance of the rain- and drain-gauges, and the experimental wheat field at Rothamsted, the character of the waters from which we have already considered. Harpenden is situated about 25 miles to the north of London. The village occupies a small valley. The centre of the village, according to the Ordnance Survey, is about 344 feet above the level of the sea; the high ground on the west, or Rothamsted side, rises to about 430 feet, and that on the east to 415 feet. The soil in the valley is more or less gravelly; on the hills, on each side, the surface soil is clay mixed with flints. Below the surface soil comes in every case the chalk; this is in some places quite near the surface, and in other cases as much as 25 feet below. All the wells are sunk into the chalk.

The height of the water in the wells is of course subject to variation at different times of the year, but it may be generally stated that in the centre of the village the water level is rather less than 60 feet below the surface. The extreme depth is reached in well C, situated on the high ground on the east of the valley; the water level is here about 145 feet below the surface.

In the valley the water level in the wells is about 290 feet above the sea level. In the wells on the high ground to the west (the Rothamsted side) the water level is distinctly higher; while in well C, on the east hill, the water level is distinctly lower than in the valley. There is thus a steep gradient in the water level from north to south, that is between Harpenden and the centre of the Thames valley; and also in the direction of west to east. The existence of these steep gradients will of course determine a steady flow of the underground water in the directions indicated. This fact is one of primary importance, and must be borne in mind when we have to study the alterations in the composition of the well waters.

The waters of about 30 wells, in or near the village of Harpenden, have been examined, and a few others from the neighbourhood. The examination has generally been of a very simple description; it consisted of a quantitative determination of chlorine and nitric acid,* and in the case of suspected waters of a qualitative examination for ammonia and nitrous acid. Samples of water giving distinctly the reaction of ammonia, or containing nitrous acid, have been rare; with such waters we shall have nothing to do in the present report. Our attention will be confined to the proportion of chlorine and nitric acid in well waters which contain no appreciable amount of ammonia; and it will be our main object to inquire what are the facts which the varying quantities of chlorides and nitrates indicate.

The examination of well waters in Harpenden was commenced with no intention of making a systematic study, but simply with the object of satisfying individual householders as to whether their well was contaminated by sewage. As results accumulated, it was found that the composition of many well waters varied considerably at different seasons of the year. Certain wells were then selected for systematic examination, and determinations of the chlorine and nitric acid in their water were made every month; the samples were collected about the 20th day of the month. The systematic examination of those selected wells has been continued during two years. The results yielded by those wells which have been repeatedly examined will be found in the tables on pp. 524—529.

---

* Chlorine was determined volumetrically. Nitric acid was determined by the improved indigo method.—*Trans. Chem. Soc.*, 1879, 578.

Before considering the composition of the well waters, it will be desirable to have a clear idea as to the sources of the water which these wells contain. What has been already stated respecting the gradients of the water level, and the movement of the underground water which these gradients indicate, will have established the fact that the constant supply of water to the deep wells of Harpenden is derived from the drainage of a district to the north-west of the village, and is thus independent of the local drainage. In the case of most deep wells there will probably be a similar independence of local drainage for the constant water supply of the well. This constant underground supply of water to deep wells, being the result of percolation over a wide area, and through a great depth of soil, we should expect to have a constant composition throughout the year.

Besides the main water supply derived from a large area, and presumably of constant composition, there will in nearly every case be more or less of local drainage. This local drainage will be determined by any preceding rainfall sufficient to supersaturate the surrounding soil, and will occur to its greatest extent between the months of October and February. If this local drainage percolates through a very considerable depth of soil before entering the well, it will supply a water of nearly constant composition, and any alteration in composition which the admixture of this water may determine will be in the same direction at whatever time of the year the local drainage may occur. If, however, as must frequently be the case, the local drainage finds access to the well not far below the surface, or through deeper channels coming directly from the surface, the composition of the local drainage will be different at different seasons of the year—as indicated by the facts established earlier in this report by a study of land drainage waters—and the composition of the well water may consequently alter in more than one direction in the course of the year.

The composition of the local drainage will of course vary immensely according to the condition of the soil supplying this drainage. The soil around the well may be uncropped and unmanured—a gravelled yard for instance—in which case the character of the drainage will assimilate to that of the drainage from the Rothamsted drain-gauges containing bare soil. Or it may be cropped garden ground, more or less manured, in which case the composition of the local drainage will vary at different seasons in the direction shown by the drainage waters from the Rothamsted wheat field. Or lastly, the neighbouring soil may be contaminated with excrementitious matter, either the drainage from stables or human sewage, the latter distinguished by its large contents of common salt. In either case the local drainage will be of a far more concentrated character than under the previously named conditions.

The views we have here expressed respecting the sources of the water supply to deep wells, and regarding the circumstances which will determine the constancy or variation in the composition of the well water, will, we think, be justified by the facts to which we have now to call attention.

The Generally Uncontaminated Well Waters.

To form a correct judgment of any local water supply we must first know what is the composition of the pure waters of the district. It is obvious from the facts already mentioned, respecting the composition of land drainage waters, that not the whole of the chlorides and nitrates in a water is to be reckoned as derived from previous sewage contamination. If, however, the composition of the pure well waters of a district is known, a distinct excess of chlorides and nitrates in any particular water will indicate with considerable certainty contamination by sewage.

Among the "generally uncontaminated" well waters mentioned in Tables VII—IX there are two, A and C, which have never shown during two or more years of investigation any sign of sewage contamination. Well A is on rising ground from the village, its water level will be about 70 feet below the surface. Well C is on the east hill, and has a water level about 145 feet from the surface; from this well a general water supply for the village is at present being arranged. The amount of chlorine in the water from A, on an average of 30 monthly determinations, spread over seven years, is 10·8 per million. The proportion of chlorine is practically constant at all times of the year; the whole variation during the last two years of systematic observation has been from 10·7 to 11·3. The far deeper well C gives on an average of 20 monthly determinations 11·6 of chlorine per million of water. Here, too, the amount of variation has been extremely small. The slightly higher proportion of chlorine is possibly due, as we shall see bye-and-by, to the greater depth of the well.

There is abundant evidence that the normal proportion of chlorine in the pure well waters of the Harpenden district is about 11 per million. The water from wells B and D, which are generally uncontaminated, shows this proportion at most seasons of the year. While of the contaminated wells, not a few, as F, G, H, and J, reach more or less nearly this figure, after a long continuance of dry weather has stopped the source of local contamination. The evidence in favour of

TABLE VII.—*Chalk Well Waters, Harpenden, Herts. Chlorine per Million of Water.*

		Generally uncontaminated.					Generally contaminated.								
		A.	B.	C.	D.	E.	F.	G.	H.	J.	K.	L.	M.	N.	O.
1879.	June......	11·3	—	—	—	—	—	—	—	—	—	—	—	—	—
1880.	February..	—	—	—	—	—	47·0	—	—	—	—	—	—	—	—
1881.	July......	11·1	—	—	—	—	—	—	—	—	16·0	—	—	—	—
1882.	April.....	—	11·7	—	—	—	21·2	—	17·7	22·1	—	—	—	—	—
	May......	—	—	—	—	—	—	—	—	—	—	—	—	—	24·3
	July......	—	—	—	—	—	—	—	—	—	—	—	—	—	25·5
	November.	—	—	—	—	—	—	—	—	—	—	—	57·0	—	—
1883.	March....	9·8	—	—	—	—	62·6	—	—	—	—	—	—	—	—
	May......	—	12·4	—	—	—	25·2	—	—	—	—	—	—	—	—
	November.	10·6	10·9	—	—	12·1	15·4	—	11·7	12·4	14·5	—	33·4	—	—
1884.	March....	9·6	10·1	—	—	—	—	—	11·7	—	—	—	36·5	—	—
	April.....	—	—	—	—	—	—	11·1	—	—	—	—	—	—	—
	October...	—	10·6	—	—	—	11·9	—	11·3	12·0	—	—	27·7	—	—
	December.	—	—	—	—	—	—	—	—	—	—	—	24·7	—	—
1885.	February..	10·7	11·0	11·1	—	14·7	10·6	—	12·0	—	—	15·0	36·1	—	20·6
	March....	11·3	11·4	—	—	—	—	—	13·0	17·2	24·2	62·0	40·2	—	22·0
	April.....	11·1	—	—	—	13·2	—	—	14·1	14·8	15·6	49·2	35·7	—	22·8
	May......	—	11·1	10·8	—	—	—	—	14·2	14·8	15·7	57·4	36·8	—	22·7
	June.....	11·0	—	—	—	—	13·2	—	15·4	17·3	18·3	65·7	36·6	—	22·3
	July......	11·3	—	12·0	—	13·0	—	—	13·8	17·5	17·2	56·0	35·4	—	23·0
	September.	10·3	10·8	11·1	11·2	12·8	—	—	12·9	17·0	16·3	37·5	36·1	—	22·4

TABLE VII—*continued.*

		Generally uncontaminated.					Generally contaminated.								
		A.	B.	C.	D.	E.	F.	G.	H.	J.	K.	L.	M.	N.	O.
1885.	October ...	10·9	—	—	11·3	—	—	—	13·0	17·8	19·0	31·6	39·8	—	22·3
	November .	11·1	11·4	11·3	11·9	13·2	—	—	13·6	21·7	24·5	49·2	56·0	—	22·0
	December..	10·9	12·9	—	12·5	—	—	15 9	17·1	21·6	19·9	64·1	62·6	—	23·2
1886.	January ..	10·9	—	11·7	12·6	13·8	—	—	18·1	26·4	17·2	47·1	60·0	—	23·6
	February..	10·7	13·0	—	13·7	—	—	—	23·9	32·7	20·5	36·2	71·0	—	24·1
	March	10·8	14·2	11·9	14·0	19 2	—	19·9	25·5	30·7	19·7	29·9	79·3	—	24·8
	April	10·8	12·8	12·0	13·6	14·5	—	—	21·5	26·8	19·7	25·7	70·3	—	24·8
	May	10·9	11·8	11·6	12·9	13·6	—	—	19·0	22·7	19·9	23·3	60·6	—	24·1
	June......	11·0	12·7	11·5	13·4	14·3	—	—	20·1	23·7	19·4	23 8	70 0	—	23·9
	July......	11·0	12·0	11·8	13·1	15·1	—	—	17·9	20·3	18·0	21·1	60·5	—	23·9
	August....	11·0	11·5	11·8	12·4	14·1	—	—	15·8	17 0	17 3	18·4	48·9	138 6	24·0
	September.	10·9	11·2	11 7	11·9	13·3	—	—	14·1	13·7	16 5	21·5	45·3	130·6	24·0
	October ...	10·9	11·0	11·4	11·7	13·4	—	12·5	13·2	13·9	16·4	25·5	42·8	139·2	23·3
	November .	10·8	11·0	11 8	11·7	14·0	—	—	13·2	16·5	17·0	26·4	45 9	153·2	22·9
	December .	10·9	11·0	11·4	11·7	14·1	—	—	13·6	16·3	17·5	32·2	52·1	161·2	23·0
1887.	January. .	10·7	13·8	11·7	12·8	14·7	—	—	19·2	22·4	18·9	46·4	55·7	163·0	23·2
	February .	10·8	16·4	11·6	14 6	24·2	—	—	30 8	32·1	18·8	30·9	77 3	173·2	23 6
	March	10·8	13·0	11·7	14·0	19·5	—	—	28·5	29 3	18·6	25·5	86·9	155·2	24·1
	April	10·9	12·2	11·7	13·4	13·9	—	—	23·5	24·9	18·6	21·5	72·7	141·0	24·0
Mean of all.....		10·8	12·2	11·6	12·7	14·8	25·9	14·9	17·0	20·6	18·3	36·3	51·5	150·6	23·4
Mean of 12. May, 1886—April, 1887		10·9	12·3	11·6	12·8	15·4	—	—	19·1	21·1	18·1	26·4	59·9	—	23·7

TABLE VIII.—*Chalk Well Waters, Harpenden, Herts. Nitrogen as Nitrates per Million of Water.*

	Generally uncontaminated					Generally contaminated							
	A.	B.	C.		E.	F.	G.	H.		K.		M.	
January									—				
April ..						7 9		8·1	11·4				
May ...						—		—	—				9·0
July ...						—		—	—				8·5
Novemb						—		—	—	—		17·0	—
Novemb		4·7			4·8	6 2	—	5·0	5·3	7·7		16·1	—
March .		4·8			—	—.	—	5·7	—	—		15·8	—
April...		—			—	—.	4·9	—	—	—		—	—
October		4·4			—	4 7	—	4·5	4·3	—		10·7	—
Februar	4·5	4·7	5·4		4·9	4 8	—	4·9	—	—	5·6	12·0	8·3
March .	4·6	4·6	—		—		—	5·4	7·2	14·0	23·6	13·1	8·6
April ..	4 6	—	—		4·8		—	5·8	7·0	7·9	19 7	11·4	8·6
May	—	4·5	5·2		—		—	5·8	7·2	8·1	22·6	11·5	8·6
June....	4·4	—	—		—		—	6·4	8·1	9·7	26·2	11·3	8 6
July ...	4·4	—	4·9	—	4·7		—	5·8	7·8	9 0	21·8	11·2	8 1
Septemb	4·5	4·5	5·3	4·7	4·8		—	5·0	7·2	8·1	13·3	11·1	8·4
October	4·5	—	—	4·6	—		—	5·3	7·4	10·3	11·5	11·7	8·5
Novemb	4·5	4·5	5·3	4·9	5·1		6·6	5·6	9·5	13·8	18·1	15·6	8·6
Decembe	4·6	5·2	—	5·3	—		—	7·5	11·3	11·5	32·8	17·3	9·3
January	4·7	—	5·4	5·4	5·4		—	8·4	14·9	9·7	26 9	17·0	9·5
Februar	4·9	6·9	—	6·2	—		8·6	.1·6	21·3	12·5	21·0	19·3	9·8
March ..	5·2	5·8	5·7	6·7	.0·3			.2·5	20·5	12·2	16·3	21·9	.0·1

TABLE VIII—*continued.*

		Generally uncontaminated.					Generally contaminated.								
		A.	B.	C.	D.	E.	F.	G.	H.	J.	K.	L.	M.	N.	O.
1886.	April.....	5·0	5·3	5·6	6·4	6·7	—	—	10·7	17·5	12·4	14·0	21·5	—	10·0
	May......	4·9	5·1	5·3	5·7	5·4	—	—	8·8	13·7	11·7	11·6	17·8	—	9·4
	June......	4·8	5·1	5·3	6·1	5·3	—	—	9·1	13·9	11·2	11·7	19·8	—	9·2
	July	4·6	4·8	5·1	5·5	5·3	—	—	8·0	11·1	9·8	9·8	17·5	—	8·9
	August....	4·5	4·6	5·1	5·1	4·9	—	—	6·7	8·6	9·1	8·3	15·5	35·7	8·8
	September .	4·6	4·6	5·3	5·0	4·7	—	—	6·0	6·4	8·9	8·9	14·8	32·7	8·8
	October...	4·5	4·5	5·2	4·9	4·5	—	4·9	5·5	6·1	8·8	10·8	14·4	35·9	8·6
	November .	4·5	4·5	5·2	5·0	4·4	—	—	5·4	7·0	9·6	11·0	14·7	39·4	8·8
	December*	4·4	4·4	5·1	5·0	4·4	—	—	5·7	6·8	9·5	12·9	15·9	40·9	8·8
1887.	January...	4·7	—	5·4	5·8	4·9	—	—	8·9	11·2	11·0	24·6	16·2	42·1	9·3
	February..	4·9	6·4	5·3	7·1	11·1	—	—	14·6	20·2	10·5	16·5	21·3	44·0	9·6
	March	5·1	5·2	5·2	6·7	7·9	—	—	14·0	18·9	10·2	13·1	25·1	40·5	9·7
	April	4·8	4·9	5·2	6·1	5·0	—	—	11·1	14·7	9·8	10·4	21·4	36·0	9·2
Mean of all		4·7	5·0	5·3	5·6	5·7	7·2	6·3	7·6	11·0	10·3	16·3	16·0	38·6	9·0
Mean of 12. May, 1886—April, 1887		4·7	4·9	5·2	5·7	5·7	—	—	8·7	11·6	10·0	12·5	17·9	—	9·1

* The determinations of nitric acid in this month are possibly rather below the truth.

TABLE IX.—*Chalk Well Waters, Harpenden, Herts. Nitrogen as Nitrates for* 100 *of Chlorine.*

		Generally uncontaminated.					Generally contaminated.								
		A.	B.	C.	D.	E.	F.	G.	H.	J.	K.	L.	M.	N.	O.
1882.	April	47·7	—	—	—	—	37·3	—	45·8	51·6	—	—	—	—	—
	May	—	—	—	—	—	—	—	—	—	—	—	—	—	37·0
	July	—	—	—	—	—	—	—	—	—	—	—	—	—	33·3
	November .	—	—	—	—	—	—	—	—	—	—	—	29·8	—	—
1883.	November .	44·3	43·1	—	—	39·7	40·3	—	42·7	42·7	53·1	—	41·9	—	—
1884.	March	49·0	47·5	—	—	—	—	—	48·7	—	—	—	43·3	—	—
	April	—	—	—	—	—	—	44·1	—	—	—	—	—	—	—
	October ...	—	41·5	—	—	—	39·5	—	39·8	35·8	—	—	38·6	—	—
1885.	February ..	42·1	42·7	48·6	—	33·3	40·6	—	40·8	—	—	37·3	33·2	—	40·3
	March	40·7	40·3	—	—	—	—	—	41·5	41·9	57·9	38·1	32·6	—	39·1
	April	41·4	—	—	—	36·4	—	—	41·1	47 3	50·6	40·0	31·9	—	37·7
	May	—	40·5	48·1	—	—	—	—	40·8	48·6	51·6	39·3	31·0	—	37·9
	June......	40·0	—	—	—	—	34·1	—	41·5	46·8	53·0	39·9	30·9	—	37·7
	July	38·9	—	40·8	—	36·1	—	—	42·0	44·6	52·3	38·9	31·6	—	35·2
	September .	41·7	41·7	47·7	42·0	37·5	—	—	38·8	42·4	49·7	35·5	30·7	—	37·5
	October ...	41·3	—	—	40·7	—	—	—	40·8	41·6	54·2	36·4	29·4	—	38·1
	November .	40·5	39·5	46·9	41·2	38·6	—	—	41·2	43·8	56·3	36·8	27·9	—	39·1
	December..	42·2	40·3	—	42·4	—	—	41·5	43·9	52·3	57·8	51·2	27·6	—	40·1
1886.	January ...	43·1	—	46·1	42·9	39·1	—	—	46·4	56·4	56·4	57·1	28·3	—	40·3
	February ..	45·8	38·3	—	45·3	—	—	—	48·5	65·1	61·0	58·0	27·2	—	40·7
	March	48·2	40·8	48·0	47·9	53·6	—	43·2	49·0	66·8	61·9	54·5	27·6	—	40·7
	April......	46·3	41·4	46·7	47·1	46·2	—	—	49·8	65·3	62·9	54·5	33 6	—	40·3
	May	45·0	43·2	45·7	44·2	39·7	—	—	46·3	60·4	58·8	49·8	29·3	—	39·0
	June......	43·6	40·2	46·1	45·5	37·1	—	—	45·3	58·7	57·7	49·1	28·3	—	38·5

TABLE IX—*continued.*

	Generally uncontaminated.					Generally contaminated.								
	A.	B.	C.	D.	E.	F.	G.	H.	J.	K.	L.	M.	N.	O.
1886. July	41·8	40·0	43·2	42·0	35·1	—	—	44·7	54·7	54·8	46·4	28·9	—	37·2
August....	40·9	40·0	43·2	41·1	34·8	—	—	42·4	50·6	52·6	45 1	31·7	25·8	36·7
September.	42·1	41·1	45·3	42·0	35·3	—	—	42·6	46·7	53·9	41·4	32·7	25·0	36·7
October ...	41·3	40·9	45·6	41·9	33·6	—	39·2	41·7	43·9	53·7	42·4	33 6	25·8	36·9
November .	41·7	40·9	46·0	42·7	31·4	—	—	40·9	42·4	56 5	41·7	32·0	25·7	38·4
December..	40·4	40·0	44·8	42·7	31·2	—	—	41·9	41·7	54·8	40·1	30·5	25·4	38·3
1887. January ...	43·9	—	46·2	45·8	33·3	—	—	46·8	50·0	58·2	58·0	29·1	25·8	40·1
February ..	45·4	39·0	45·7	48·6	45·9	—	—	47·4	62·9	55·9	53·4	27·6	25·4	40·6
March	47·2	40·0	44·4	47 9	40·5	—	—	49·1	64·5	54·8	51·4	28·9	26·1	40·2
April	44·4	40·1	44·4	45·5	36·0	—	—	47·2	59·0	52·6	48·4	29·4	25·5	38·7
Mean of all.....	43·2	40·6	45·7	43·9	37·8	38·4	42·0	44·0	51·0	55·5	45·4	31·2	25·6	38·4
Mean of 12. May, 1886—April, 1887	43·1	40·5	45·1	44·1	36·2	—	—	44·7	53·0	55·8	46 9	30·2	—	39·0

this minimum figure is still greater if we take into account the analyses of other Harpenden well waters not mentioned in the foregoing tables. Under this head the following may be quoted:—

TABLE X.—*Individual Analyses of Uncontaminated Well Waters. Harpenden, Herts.*

Well.	Date of analysis.	Chlorine per million.	Nitrogen as nitric acid per million.	Nitrogen to 100 chlorine.
R..........	1880, February.........	10·2	—	—
S..........	1882, May	10·4	—	—
T..........	1883, August	11·0	—	—
U..........	1884, July	10·1	4·7	46·5
V..........	1885, February	11·0	4·5	40·9
W	„ December	10·9	4·5	41·3
DD	1886, August	11·6	4·4	38·0
FF	„ „	10·7	4·5	42·1
	Mean............	10·7	4·5	41·8

There is one well, E, classed as "generally uncontaminated," the water of which usually contains 13—14 of chlorine per million, even after a long continuance of dry weather. This well is the only one in Harpenden terminating in a boring. The main shaft is about 58 feet deep, the boring extends an additional 156 feet, or 214 feet in all. As this well is situated in the valley, the water is collected from a far greater depth in the chalk than is the case with any other well examined. Large quantities of water are pumped from the well, which belongs to a brewery. The proportion of nitrates is generally that found in the purest of the well waters, and affords strong evidence that the well, save under exceptional circumstances, is uncontaminated. The reason of the distinctly larger proportion of chlorides in this well water is, I believe, the greater depth in the chalk from which the water is derived; this point will be further discussed later on.

The average amount of nitrogen as nitrates in the pure water of well A is seen from Table VIII to be 4·7 per million. Nearly the same amount is contained in the water of well B, save in the few months in which it was plainly contaminated. The more frequently contaminated well waters, D, F, G, H, J, show a similar proportion of nitrates when in their purest state. The individual analyses of pure waters, given in Table X, confirm the same proportion. We may therefore adopt 4·7 per million as the average amount of nitric nitrogen in the pure well waters of Harpenden. The only pure well giving a somewhat higher figure is C.

The proportion of nitrates is not, as is the case with the chlorides, perfectly constant throughout the year in the waters of all uncontaminated wells. In the waters of wells A and C, the quantity of nitrates, and their proportion to the chlorides, increases slowly as the drainage period advances, the maximum being reached in March or April. This increase of nitrates is due to local drainage. The surrounding soil produces nitrates in summer, which during the winter drainage enter the well; no distinct amount of chlorides enters with the nitrates, the surrounding soil being uncontaminated by sewage.

The amount of total solid matter, and of lime, magnesia, silica, sulphuric and carbonic acids, in the uncontaminated water of well A will be found on p. 543.

The analysis of the pure well waters furnishes us with evidence as to the average composition of land drainage water, collected from a large area, and percolated to a depth exceeding 60 feet. Such water apparently contains no more than 11 per million of chlorine, and 4·7 per million of nitrogen as nitrates. We have already had reason to believe that the chlorine in the land drainage water is probably somewhat less than here indicated. The nitric nitrogen should rather be taken as 4·4 per million, the *minimum* amount occurring in the pure well waters. The average contents of drainage water in nitrates is a fact of considerable agricultural importance; it enables us to estimate the loss of nitrogen which land suffers by drainage. Taking the nitric nitrogen as averaging 4·4 per million of drainage water, it would appear that in the drainage area supplying the Harpenden wells there is an average loss to the soil of 1 lb. of nitrogen per acre for each inch of drainage. The average annual loss to the soil by drainage in this district is thus very probably 5—8 lbs. of nitrogen per acre.

The Generally Contaminated Well Waters.

The waters in these wells are held to be contaminated because the proportion of chlorides and nitrates which they contain is generally considerably above that belonging to the purest well waters of the neighbourhood, and we may consequently conclude that they are polluted by the products of the oxidation of sewage present in the surrounding soil. The wholesomeness, or unwholesomeness, of these waters containing oxidised sewage is a subject beyond the scope of the present paper; we may, however, remark that during the time of the current investigation they were drunk apparently with impunity.

The circumstances which determine contamination or purity are so special that it is unsafe to predict from the surroundings of a well whether the water will be found pure or not. Thus, well B is a very old well, surrounded by cottages; its mouth is only two or three yards from the urinal of a small public house; yet its water usually reaches the full standard of purity, and has not unfrequently been employed at the laboratory as especially suitable for the preparation of water free from ammonia. Under exceptional circumstances this well becomes contaminated to a moderate extent, but quickly recovers itself. Wells D and M are good illustrations of the immense influence of purely local conditions. Well D is between 40 and 50 years old, it is only a few yards from the urinal and privies of a large National School, yet the contamination it suffers never exceeds a trifling amount. Well M is only about 20 yards from well D; it was sunk in the summer of 1882, and was found in November of the same year to be highly contaminated, the chlorine amounting to 57 per million of water. At the end of the driest season the water of this well is still far removed from the standards of purity, the lowest chlorine found being 24·7, and the lowest proportion of nitric nitrogen 10·7 per million of water.

The injury which any source of contamination may inflict on a well is of course largely determined by the relation of its position to the direction in which the underground water flows. With a flow of underground water from north-west to south-east, it is obvious that any soakage of sewage to the north-west of the well will probably considerably affect the water supply, while a similar soakage on the south-east side of the well will have practically no effect.

Wells are generally ill-provided with any protection to prevent soakage through their walls. The old wells of Harpenden are steined with flint, laid in hard mortar or cement, and this steining is often carried to a considerable depth. This plan appears far better than the modern one of steining with loose brick, without any cementing material.

The amount of water taken from a well must largely influence its *apparent* degree of contamination. The local contaminated drainage is strictly limited in quantity, the underground supply of pure water is practically unlimited in amount; by continuous pumping the proportion of impurity in the water may thus be greatly diminished.

The proportion of chlorine in the contaminated well waters varies of course immensely in different wells, according to the amount of sewage contaminated; it is in the better wells sometimes as low as 11 per million, the standard of purity in this district, and rises in the case of one well as high as 173 per million. The marked characteristic of the chlorides in a well water receiving fresh contamination is that they are a *variable quantity* at different seasons; while the amount of chlorides in a well water not suffering from new contaminations of sewage is practically constant. It follows that the ascertained purity of a well water at one season of the year may be no proof of its general freedom from sewage contamination. The water of well O shows a nearly constant, but high proportion of chlorides throughout the year; we will consider this apparent exception after discussing the cause of the alteration in the proportion of chlorides which the other well waters exhibit.

To understand the rise and fall of chlorides and nitrates in a well water, we must first study the amount of drainage through the soil taking place during the season in question. The amount of water passing through the deepest of the Rothamsted drain-gauges, containing 5 feet of bare soil, during each month of the several years in which the well waters have been examined, is shown in Table IV. In using this table it must be recollected that the summer drainage shown by the bare soil in the drain-gauge will be considerably in excess of the drainage taking place at the same time on ordinary land covered with vegetation. The amount of winter drainage will be nearly the same on all soils.

Periods of minimum chlorine in the waters of the contaminated wells are seen from Table VII to have occurred on or about November, 1883; October to December, 1884; September, 1885; and September and October, 1886. A reference to Table IV will show that each of these dates of minimum chlorine occurred at the end of a period of dry weather. Of these yearly minimums, that at the close of 1884 is the lowest. The dry spring, and somewhat dry summer of 1883, were followed by a dry winter, and this again by the dry spring and summer of 1884. The winter drainage of 1884–5 did not commence till late in the season. There had thus been an unusually long period of comparatively dry weather previously to December, 1884. The local drainage through the soil having thus ceased, or been reduced to a minimum, fresh contamination by the percolation of sewage was suspended, and the supply of water to the wells being thus limited to the flow of pure underground water, the chlorides and nitrates were reduced nearly to the proportion found in uncontaminated well waters, save in cases where probably the soil had become saturated to a great depth with sewage products, and when consequently chlorides and nitrates would continue to enter in limited quantities by diffusion, after direct percolation from the surface had ceased.

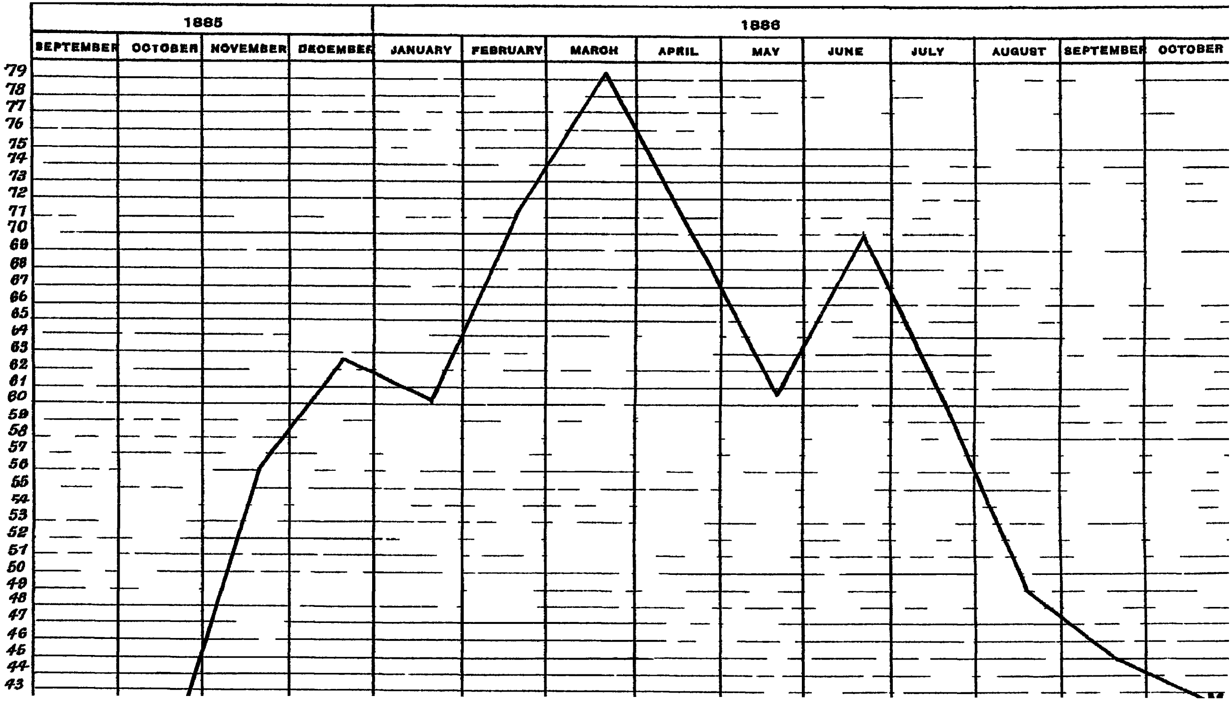
Starting from the period of minimum contamination with chlorides and nitrates in the autumn months, the figures in Tables VII and VIII show that a very considerable rise in the proportion of these salts occurs during the winter months; a maximum is generally reached in February or March, and the amount then slowly declines till the minimum is again reached in the autumn.

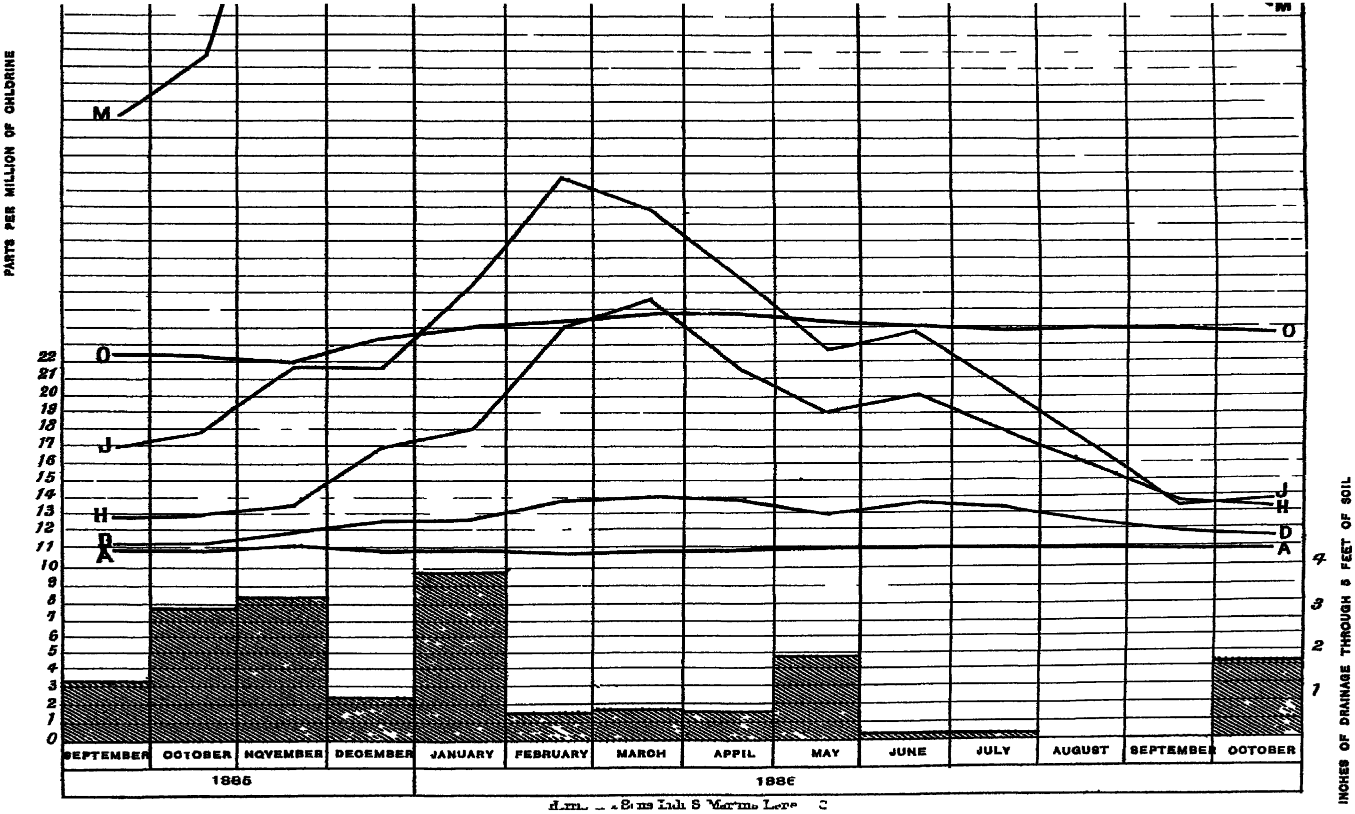
The three Charts which follow, show in a graphical form the movements which the proportions of chlorine and nitric nitrogen in six typical well waters exhibited between the period of minimum impurity in September, 1885, and the next period of minimum impurity in October, 1886. At the foot of each Chart, the amount of drainage taking place at the same time through the 5-foot drain-gauge at Rothamsted is depicted. The season selected for graphic illustration is in many respects a typical one. The rainfall was above the average, and with the exception of a heavy fall in May, was distributed throughout the season in a fairly normal manner. The drainage season commenced in September, 4·4 inches of rain fell in this month; the soil being then dry, only a small part of this rain (1·25 inch) passed through the 5 feet of soil in the drain-gauge. A wet October (rain 4·82 inches), and November (rain 3·78 inches), followed the wet September. The chlorides and nitrates in the waters of wells H, J, K, M, showed a slight rise when determined on October 21st. By November 23rd the rise of chlorides and nitrates in the contaminated wells was in nearly every case considerable.

Before pursuing the course followed by the rise of chlorides and nitrates in the well waters, it will be advisable to mention what is known as to the commencement of the rise in the water level in the wells. The only well of which I have a pretty continuous record of the water level is well C, the most easterly of the wells examined. On November 23rd, 1885, the water level in this well had not begun to rise, but by December 3rd a rise of 4 inches had taken place. A further rise of 2 inches was observed on December 7th. On January 5th an additional rise of 17 inches was recorded. The highest level (3 feet 5 inches above the minimum) was reached in March. If we may assume that the rise of water in the polluted wells in the village was contemporaneous with the rise of water in well C on the hill (the distance between them would be less than half a mile), it follows that new pollution set in before the water level in the wells began to rise. The same fact was observed in the following year. The chlorides and nitrates had been rising in the contaminated wells during November and December, but the water level in well C did not begin an upward movement till the middle of January, 1887. These facts illustrate the independence of the source of pollution from the main water supply of the well; the latter is derived from a large drainage area, while the source of pollution is purely local. The chlorides and

Ic So. June 1887

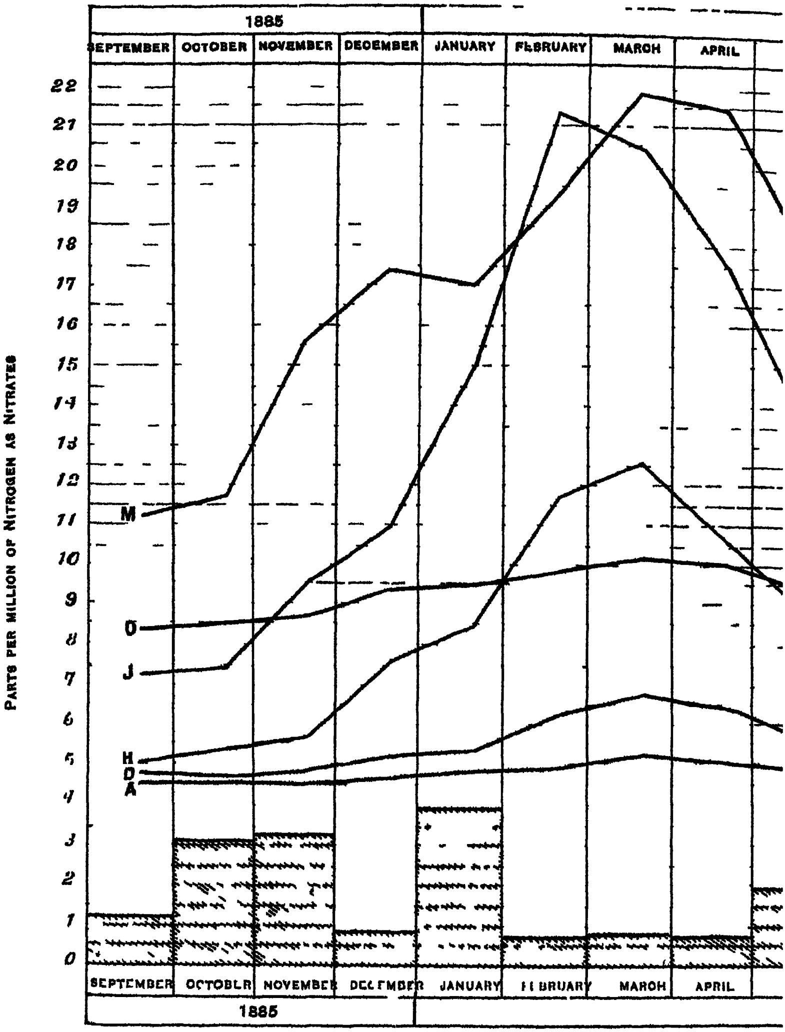
HARPENDEN WELL WATERS—CHLORINE PER MILLION OF WATER




PARTS PER MILLION OF CHLORINE
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
M
O
J
H
D
A
INCHES OF DRAINAGE THROUGH 5 FEET OF SOIL
4
3
2
1
SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER
JANUARY
FEBRUARY
MARCH
APRIL
MAY
JUNE
JULY
AUGUST
SEPTEMBER
OCTOBER
1885
1886
Sons Lith S Martins Lane

Journ Chem Soc June 1887

HARPENDEN WELL WATERS—NITROGEN AS NITRA

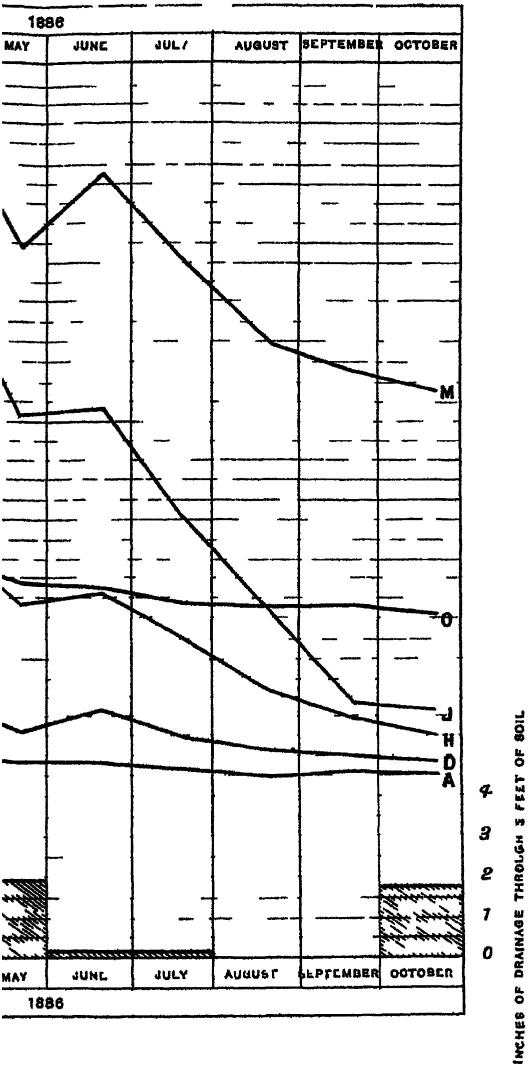


Warington—Plate F

[illegible] Lith Martin

To face page 534 2

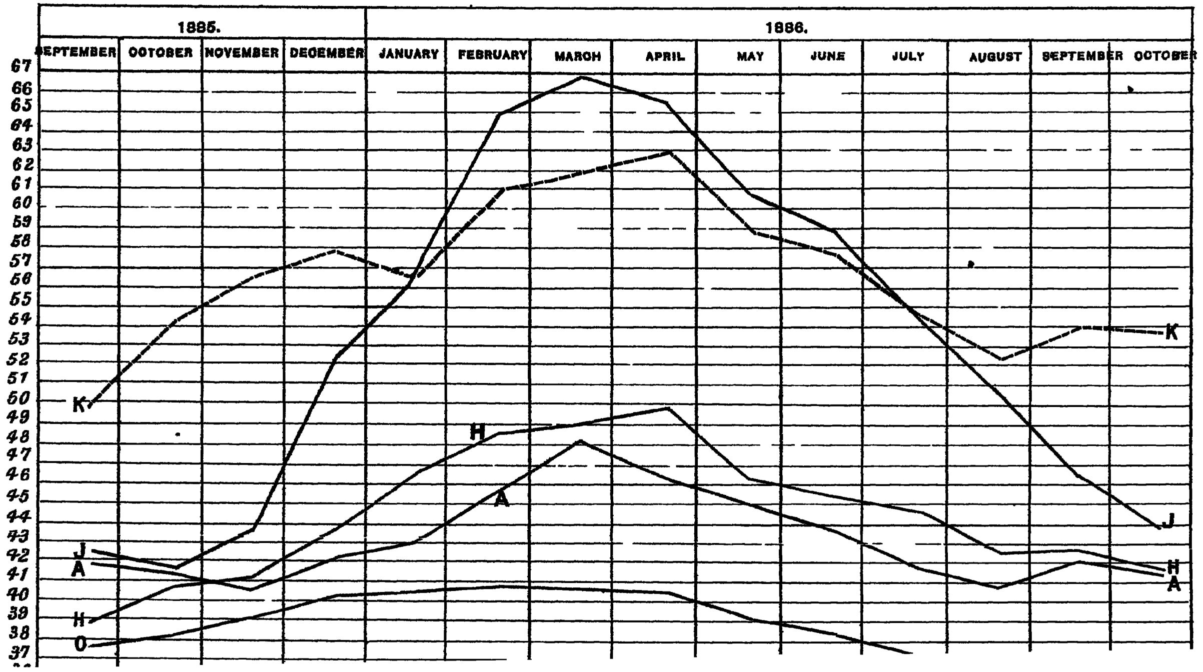
TES PER MILLION OF WATER

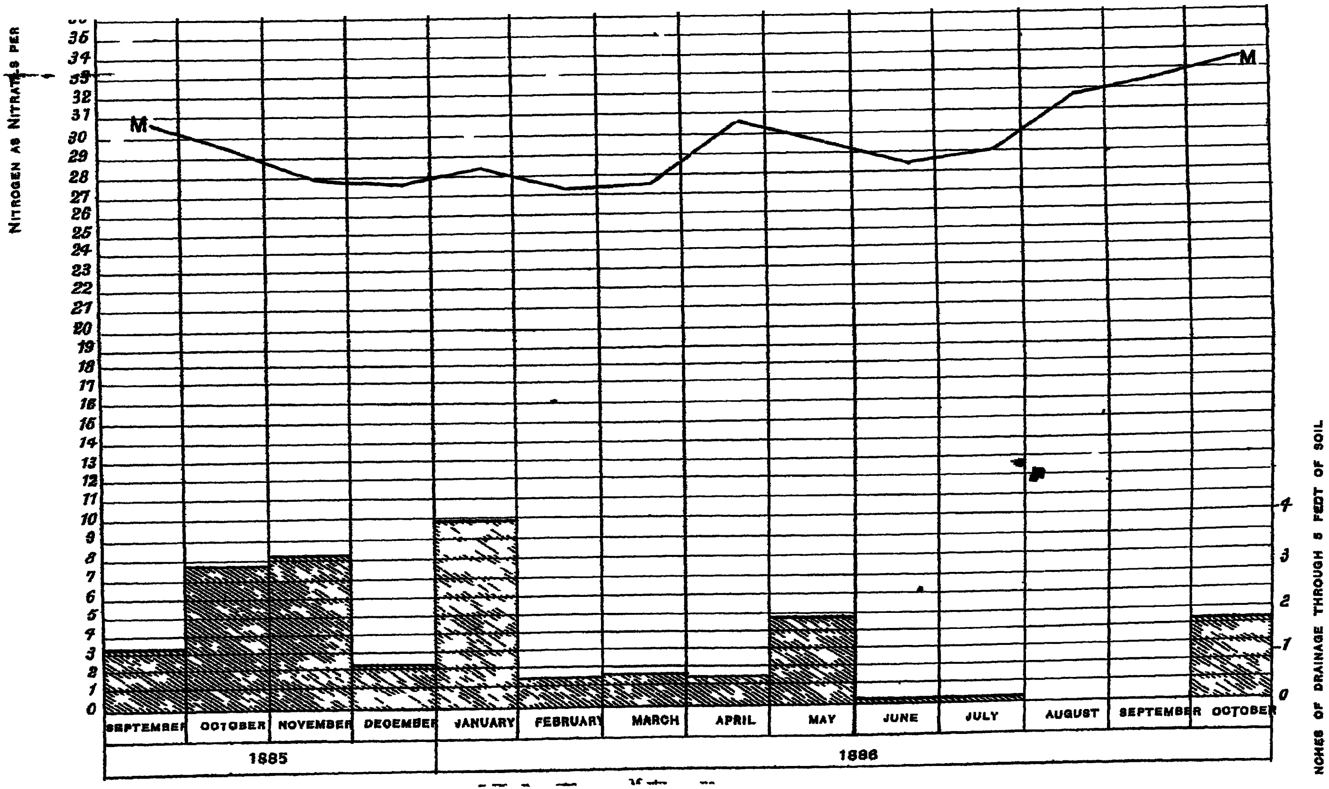


Journ Chem Soc June 1887

To face page 534-3

HARPENDEN WELL WATERS—NITROGEN AS NITRATES PER 100 CHLORINE.




NITROGEN AS NITRATES PER
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
M
M
NCHES OF DRAINAGE THROUGH 5 FEET OF SOIL
0
1
2
3
4
SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER
JANUARY
FEBRUARY
MARCH
APRIL
MAY
JUNE
JULY
AUGUST
SEPTEMBER
OCTOBER
1885
1886

nitrates of local drainage are probably in most cases discharged into the well at no great distance from the surface.

The general facts respecting the progression of chlorides and nitrates in the waters of contaminated wells during a whole season, will be best seen by looking at the mean results of several wells, simultaneously examined. In Table XI the mean proportion of chlorine found in the waters of wells H, J, K, L, M, in September, 1885 (the month of minimum chlorides), is taken as 100, and the mean proportion of chlorine found in subsequent months of the same season is expressed in relation to this standard. The nitrogen as nitrates present in the waters in September is equally taken as 100, and the subsequent rises of nitrates expressed in reference to this basis. Similar calculations have been made for a part of the season 1886–7, the mean amount of chlorine and nitric nitrogen found in September, 1886, being taken as 100.

No considerable rise in chlorides or nitrates above the autumn minimum occurs in either season till after two consecutive months of active drainage. After the soil has become saturated, the effect of heavy rain is sooner manifested; but even then it is clearly the amount of the *previous*, and not that of the present rain, which determines whether or not there shall be a further rise in impurity. The effect of the dry December, 1885, and of the wet January and May, 1886, on the amount of chlorides and nitrates in the waters of the next following months, is plainly shown in the accompanying Charts. The effect of rain is much increased when it is continuous. In the season 1885–6, there were four months of active drainage, but only three of these were consecutive. In the following season there were four months (October—January) of consecutive drainage; and although the total drainage from September to February was in the first season 13·14 inches, and in the second season 10·84 inches, the smaller drainage of the second season determined a rather higher proportion of chlorides in the well waters than was reached in 1885–6. The generally small rise of chlorides in the waters during the previous season, 1884–5, may be explained on the same grounds; the drainage from September to February was in this case 10·03 inches, but it included only three months of effective drainage. When the previous rainfall has been very large, the impurity in the water may continue to rise for two months after all drainage through the 5 feet drain-gauge has ceased, but usually the influence of one month's rainfall is expended in the course of the following month.

The figures in Table XI, referring to the progression of nitrates, show that during the first three months of active drainage the proportion of nitrates rises at about the same rate as the proportion of chlorides; when, however (as in the seasons 1885–6 and 1886–7, but

TABLE XI.—*Progression of Chlorides and Nitrates in Contaminated Well Waters, the proportion in September taken as* 100; *Mean of five Wells.*

	1885–86.				1886–87.			
	Drainage through 60-inch drain gauge.	Chlorine.	Nitrogen as nitrates.	Nitrogen to 100 chlorine.	Drainage through 60-inch drain-gauge.	Chlorine.	Nitrogen as nitrates.	Nitrogen to 100 chlorine.
	inches.				inches.			
September	1·25	100	100	39·4	0·01	100	100	43·5
October	3·15	101	103	40·5	1·74	101	101	43·1
November	3·31	138	140	41·2	2·43	107	106	42·7
December	0·91	155	181	46·6	2·37	118	113	41·7
January	3·92	141	173	48·9	3·78	146	160	47·3
February	0·60	154	192	52·0	0·51	171	184	49·4
March	0·69	154	188	52·0	0·18	170	181	49·7
April	0·58	137	171	52·6	0·19	145	150	47·3
May	1·93	121	143	48·9				
June	0·10	131	147	47·8				
July	0·11	115	126	45·9				
August	0·03	98	108	44·5				
September	0·01	93	101	43·5				

not in 1884–5), active drainage continues beyond this point, a very large increase in the proportion of nitrates takes place. In 1885-6 the mean ratio of nitric nitrogen to 100 chlorine rises from 41·2 in November, to 46·6 in December, and continues to increase till a maximum of 52·6 : 100 is reached in April. In 1886–7, there is a corresponding rise from 41·7 in December, to 47·3 in January, and the ratio is still further increased in subsequent months.

To understand this large rise of nitrates, commencing after a considerable drainage from the surface has taken place, we must recollect that the autumn drainage from the surface soil, rich in nitrates formed during the previous summer, probably in very few cases finds immediate access to the well; it will, in the first place, merely displace the water existing in the subsoil, and force this into the well. If the supply of rain to the surface is steadily maintained, a band of solution rich in nitrates, continually widening by diffusion both at its upper and lower edges, will gradually descend into the subsoil, and on touching the natural lines of drainage be delivered into the well.* When drainage ceases, at the end of the drainage season, the water in the subsoil is left to equalise itself by diffusion; it has consequently ceased to possess any distinctly nitric character when drainage recommences next autumn.

It is also to be remembered, that on every fresh addition of sewage to the surface soil, the chlorides present in that sewage are at once ready for distribution by diffusion, while the ammonia present in the sewage is fixed by the soil, and does not distribute till after the process of nitrification has taken place. After vigorous nitrification has taken place during the summer months, we should expect the surface soil to contain an abnormally large proportion of nitrates to chlorides, and consequently to yield, when rain fell upon it, a descending band of solution of this character. The dissociation of the chlorine and nitrogen in ammonium chloride, when this salt is applied to the soil, is strikingly shown by the composition of some drainage waters from Broadbalk wheat field, given at the foot of Table VI (p. 517). Equal parts of chloride and sulphate of ammonium were applied to the land on October 25th, 1880; heavy rain followed. The drainage waters collected on October 27th, 28th, and 29th showed a mean proportion of 15·4 of nitric nitrogen to 100 chlorine. In the next month, when the nitrification of the ammonia had been accomplished, the proportion was 91·4 of nitrogen to 100 chlorine.

It is further to be remarked that, according to Graham, the rate of diffusion of sodium chloride is considerably greater than that of calcium nitrate;* so that if equal quantities of both salts were present in a surface soil, the chloride would distribute itself most quickly. It seems, however, doubtful how far this difference in diffusibility would affect the relative distribution of the two salts under the conditions before us, as the quantity of calcium nitrate in the soil must exceed the quantity of sodium chloride to yield the ratio of nitrogen to chlorine found in the well waters.

---

* The existence of bands of solution, descending through a soil receiving water at the surface, has been repeatedly ascertained in the Rothamsted experiments; see *Jour. Roy. Agri. Soc.*, 1881, 329—333; 1882, 15—20.

Having thus glanced at some of the facts generally observed in the case of the decidedly contaminated wells, we must next consider the somewhat numerous exceptions to these general rules, and the causes which determine these exceptions.

There is obviously a great difference as to the period of the season in which a rise of impurity commences in different wells, as shown in Tables VII and VIII. Thus the rise of chlorides sets in earliest in wells J, K, L, M, N; the rise is much slower in H; and comes later still in B and E, when in fact some of the earlier contaminated wells are getting better. A later rise of impurity may mean that the subsoil is practically uncontaminated, so that no rise in impurity occurs by a mere pressure on the subsoil water. It may mean also that the contaminated drainage enters the well at a lower level. In the case of wells B and E, however, it would appear that a certain pressure of water (perhaps sufficient to produce an overflow) is required before any impurity enters the well. In the spring of 1885, both of these wells seem to have escaped contamination.

There is also a difference to be observed in the duration of the contamination. It is obvious that if rain continues long enough, the chlorides and nitrates in the soil will be washed through, and the drainage water after a time become weaker. Such a change has not been observed, save in the case of well L; which, both in the seasons 1885–6 and 1886–7, showed an early maximum of impurity, and then proceeded steadily to improve, although active drainage still continued, and the other contaminated wells (with the partial exception of K) were getting worse. The surrounding conditions of well L have been much improved during the last three years, the water is apparently becoming purer, and the proportion of nitric nitrogen to chlorine has increased.

Wells which after a long cessation of percolation from the surface still show an abnormally high proportion of nitrates and chlorides, have clearly the subsoil contaminated to a very considerable depth; such a well, for instance, is well M. When, after the subsoil has thus become rich in chlorides and nitrates by a long period of contamination, the conditions at the surface are improved, and no fresh sewage is brought upon the soil, the surface soil will gradually become clean by the percolation of rain, and the subsoil contamination will alone remain. Such has apparently been the case with well O, the farm well at Rothamsted. This well is probably about 200 years old; the depth to the water level is about 120 feet. Large quantities of water are pumped from it for farm use. About 25 years ago the old farm buildings surrounding it were pulled down, and the pond in its neighbourhood abolished. Still later (1884) all the house and farm drainage have been conveyed to a distance, instead of being collected in a pit not far from the well. Under these altered conditions we have a well water containing about twice as much chlorine and nitrates as the pure waters of the district, but which undergoes hardly any increase or diminution of chlorides at any period of the drainage season; it appears, therefore, that no fresh contamination is now entering the well. That the high chlorides are to be reckoned as a contamination is shown by the fact that the water of well FF, on the same hill, and at no great distance, contains only 10·7 per million of chlorine, and 4·5 per million of nitrogen as nitrates.

---

* Graham found the diffusibility of 2 per cent. solutions of calcium chloride and nitrate to be very similar, and the same to hold good respecting sodium chloride and nitrate. Calcium salts were, however, much less diffusible than sodium salts.

We will now turn to some of the peculiarities of the well waters respecting the proportion of nitric acid.

The relative proportion of nitrates and chlorides is by no means the same in all the well waters, some have a decidedly chlorinous, and others a decidedly nitric character. Taking the average relation of nitrogen to chlorine during twelve months, given at the foot of Table IX (p. 529), we see that the proportion is 43·1 and 45·1 : 100 in the case of the two uncontaminated wells A and C, and 40·5 and 44·1 : 100 in the case of the rarely contaminated wells B and D; the mean for those four wells is 43·2. This may be taken as the general average for the uncontaminated wells of the district. The generally uncontaminated well E is decidedly more chlorinous: omitting two months in which the water was decidedly contaminated, the proportion of nitrogen to chlorine, during the same season, is only 34·8 : 100. The difference in this case is due simply to an excess of chlorine, the proportion of nitrates being normal; this excess of chlorine we have already attributed to the much greater depth of the well, and more will be said presently on this point.

Among the contaminated wells there are some considerable differences respecting the relative preponderance of nitrates or chlorides, resulting from the particular character of the contamination which the different wells receive. If we knew the relative volumes of the underground water supply, and of the local drainage conveying contamination, which together constitute the water of the well, we should be able to calculate in every case the special composition of the impure drainage entering the well. This, however, is not possible; we can only bear in mind that the impurity entering a nitric well must be considerably more nitric, and the impurity entering a chlorinous well considerably more chlorinous than the well water itself.

A glance at Table IX will show that the water of the moderately contaminated well K has been uniformly of a decidedly nitric character; only once during 26 months has the proportion of nitric nitrogen to chlorine been less than 50 : 100, while the average proportion has been 55·5 : 100. This well has stables in the immediate vicinity, and to this cause we may probably attribute the particular condition of the water. Common salt being no part of a horse's food, we should expect to find in stable sewage a low proportion of chlorine to nitrogen. Well J also shows a high average ratio of nitrates to chlorides, but the high proportion of nitrates occurs solely in the months of greatest contamination; after dry weather the proportion of nitrates to chlorides becomes normal. There are no stables near this well.

There are two contaminated wells in the series, M and N, the waters of which are of a decidedly chlorinous character. The average proportion of nitric nitrogen to chlorine is in the case of M 31·2 : 100, and in the case of N 25·6 : 100. A chlorinous condition may arise from several causes. The composition of the sewage may be different. The sewage from poor cottages, where salt bacon or herring is the only meat consumed, will contain a larger proportion of chlorine to nitrogen than the sewage from houses containing a well-fed population. The sewage of house drains will again be probably more chlorinous than the soakage from cesspits. A considerable alteration in the proportion of chlorine to nitrogen will also be determined by the presence of vegetation on the soil surrounding the well; the vegetation, by assimilating the nitrates, will increase the proportion of chlorides to nitrates in the drainage water. In the drainage water from 5 feet of bare soil at Rothamsted the proportion of nitric nitrogen to chlorine is 276 : 100 (Table III); in the drainage water from the wheat field the proportion is 55·8 : 100 (Table VI). There is possibly also in some cases a reduction of nitrates in the subsoil. The old sewage contamination existing in some subsoils seems to be generally chlorinous. On this head, however, the evidence is but small.

There is again a difference among the wells as to the constancy or variability of the relation of nitrogen to chlorine throughout the year. In a majority of the well waters, whether contaminated or not, there is a considerable increase in the proportion of nitrates to chlorides during the later months, December to April, of the drainage period (see Table IX and Chart next p. 535); the cause of this has been already discussed. There are wells, however, as M, N, and B, the waters of which show little if any indication of an increase in the proportion of nitrates to chlorides at this season. I am unable definitely to assign a cause for this peculiarity. I can only point out certain conditions which seem capable of producing the effect in question. A probable cause of the fact in question would be the percolation of the contaminating drainage to such a considerable depth before entering the well that it should be constant in composition throughout the year; the total quantity of impurity entering the well would still, however, vary greatly at different seasons according to the pressure put upon the subsoil water by fresh rainfall at the surface. This explanation would be in accordance with the facts shown by many of the wells in 1884–85, when in consequence of the rather small rainfall, hardly any increase in the proportion of nitrates was observed during the spring months. Apparently in this season the drainage from the surface soil never reached the well water, but the contamination was furnished solely by water previously in the subsoil.

It is curious to observe that in the case of well M the proportion of nitrates to chlorides is highest in the *autumn*, when the water is at its purest. The curve showing the variations in this proportion (Chart opposite p. 535) is in fact an inverted curve. This is apparently due to the fact that the proportion of nitrates to chlorides in the pure underground water is in this case greater than in the contaminated drainage which the well receives during the winter months; the purer the well becomes, the higher, therefore, is the proportion of nitrates to chlorides in the water.

EXAMINATION FOR NITRIFYING ORGANISMS.

The supposition that any considerable amount of nitrates is formed in the wells now under consideration, seems negatived by the fact that not more than traces of ammonia are ever present in the well waters; it seemed, however, of some interest to ascertain whether the nitrifying organism occurred in deep well waters. Experiments already published (*Trans. Chem. Soc.*, 1887, 118) show that the nitrifying organism has not been found in the Rothamsted subsoils at a depth exceeding 6 feet from the surface, and that especially the five samples of chalk taken from depths of 5—8 feet all failed to produce nitrification. It has further been ascertained by Frankland that water obtained from a great depth in the chalk is practically free from oxygen. It appears thus extremely improbable that the natural water supply in the chalk, which in the Harpenden wells is at a depth of 60—145 feet from the surface, should contain nitrifying organisms. On the other hand, it is equally clear that some surface soil will reach the bottom of the well, both during the operation of sinking, and as falling dust afterwards; in cases in which the water is raised by bucket and rope the communication with the surface is of course very frequent.

The first experiments were started in July, 1885. Eight sterilised solutions, each 100 c.c., containing ammonium chloride, potassium sodium tartrate, potassium phosphate, magnesium sulphate, and calcium carbonate, were seeded with 1 c.c. of water from wells A, C, H, J, K, L, M, and O. Examined on September 24th, after about 60 days, nitrification was found to be completed in the solutions seeded from C and L, and to have commenced in those seeded from A and H: all of these are bucket wells. Again examined in August, 1886, more than a year after seeding, the solutions seeded from wells M and O were found nitrified; in the two other solutions, seeded from J and K, a considerable ammount of ammonia still remained. The evidence thus indicated a more or less feeble development of the nitrifying organism in six cases, and its apparent absence in two.

A second series of experiments was started in August, 1886; the examination was confined to wells C, K, O, and DD, which are provided with pumps. A pint bottle, containing 20 c.c. of a sterilised ammoniacal solution, was taken to each well, and after working the pump for some time, about 300 c.c. of the water were introduced into the bottle as quickly as possible, and the cotton-wool stopper replaced. One series of solutions contained potassium sodium tartrate as before; another series of solutions contained no substance supplying organic carbon. The solutions were not examined till October 2nd, about 45 days after starting the experiment. All the solutions had then completely nitrified. A considerable amount of nitrous acid was present, which afterwards disappeared. Thus by using a large volume of the well waters their capacity for producing nitrification became plainly manifest. The previous experiments, however, plainly show that, at least in a majority of cases, the organism was either very scanty, or very feeble.

DETERMINATION OF MINERAL CONSTITUENTS.

On February 23rd, 1886, at a period of maximum pollution of the contaminated wells, samples of water were taken for analysis from the pure well A, and from two contaminated wells, J and M. The amount of solid residue, dried at 100°, yielded by a million parts of water, and its general composition, are shown in the following table:—

TABLE XII.—*Composition of Uncontaminated and Contaminated Deep Well Waters, collected February 23rd, 1886, in parts per Million.*

	Uncontaminated.	Contaminated.	
	Well A.	Well J.	Well M.
Lime	158·0	211·0	220·0
Magnesia	4·1	9·7	10·5
Sulphuric anhydride	3·8	28·5	15·8
Nitric anhydride	18·9	82·2	74·4
Carbonic anhydride	118·7	130·6	124·2
Chlorine	10·7	32·7	71·0
Silica	17·6	15·8	15·4
Undetermined	15·8	49·5	68·1
Total solids	347·6	560·0	599·4

The hardness of these waters, calculated according to the conventional manner as equivalent to grains of calcium carbonate per gallon, is for well water A, 20·5; well water J, 28·1; and well water M, 29·3.

In reviewing the constituents of these waters we see that two of them, silica and carbonic acid, are in nearly the same amount whether the water is contaminated or pure. The lime and magnesia, especially the latter, show a considerable increase in the contaminated waters; and as this increase is without any corresponding increase in the carbonic acid, it is clear that these bases are here combined with nitric, sulphuric, or hydrochloric acid, thus considerably increasing the permanent hardness of the water. It is well known that nitrification in a soil results in a solution of the bases, chiefly lime, by the nitric acid formed; we have here the results of this action. The proportion of magnesia to lime in the pure water is 1 : 39; in the *excess* present in the contaminated waters it is rather more than 1 : 10. The undetermined matter (partly combined water) undoubtedly contained alkalis, as the acids are in every case in excess of the bases determined. The alkalis, on these grounds, must have been between three and four times as much in the contaminated waters as in the uncontaminated.

The water of the uncontaminated well contains a mere trace of sulphuric acid. A second determination was made in December, 1886; this time 2 litres of water were concentrated to a small bulk in a retort before proceeding to the determination. The amount of sulphuric anhydride found by this more accurate plan was only 2·75 per million. This amount is hardly greater than that found in the rain water at Rothamsted (2·52 per million). As the rain is concentrated to at least one-third before appearing as drainage water, it is evident that a considerable part of the sulphates in rain are retained by the soil, or more probably by the vegetation growing upon it. In the contaminated waters the amount of sulphuric acid is very considerably increased, the increase being much greater in well J than in M. Well J is an old well; well M was sunk in 1884. Well J is a nitric well; well M a chlorinous. The two wells are not far apart; but the sewage affecting well J is undoubtedly derived from a much better fed population than is the case with well M. Hence the much higher proportion of nitrates to chlorides in well J, and hence also, apparently, the higher proportion of sulphates. The albuminoids of animal food have been found to be richer in sulphur than the albuminoids of vegetable food.

COMPARISON WITH RESULTS FROM OTHER WELLS.

It is clearly important to inquire how far the facts observed in the case of the deep well waters at Harpenden are shown by other investigations of deep well waters. In the Sixth Report of the Commission (1868) on the Pollution of Rivers, Dr. E. Frankland has given analyses of water from 36 springs, and 75 deep wells in the chalk. Of these, 30 springs, and 65 wells, are classed as "unpolluted." An "unpolluted" water, in the sense here intended, is one free from fresh sewage, as shown by the absence of an undue proportion of organic carbon and nitrogen, or ammonia; such a water may however contain chlorides and nitrates resulting from previous sewage contamination. This class of unpolluted chalk waters thus compares perfectly with the waters studied at Harpenden.

On looking at this valuable series of analyses, one is struck by the fact that the minimum of chlorine observed in the Harpenden well waters hardly ever occurs. Out of 111 samples of water there are only

2 containing less than 11 per million of chlorine.
3 „ 11—12 per million „
2 „ 12—13 „ „
6 „ 13—14 „ „
4 „ 14 „ „
0 „ 14—15 „ „

As many of the springs and wells examined were of the highest class, it would appear that there is some peculiarity in the chalk water of Harpenden so far as its contents in chlorides is concerned. I venture to think that the low proportion of chlorides in the pure well waters of Harpenden may be due to the situation of the village not far from the escarpment of the chalk at the northern edge of the Thames basin. The chalk here being at a considerable elevation (the locality comprising the wells is from 344—430 feet above the sea), and the gradient of the underground water level very considerable, the chalk rock has been in the course of ages washed very thoroughly by the percolation of rain, and the chlorides originally present in the rock when upheaved from the sea have been almost completely removed. The wells in the lower part of the chalk basin are obviously supplied to a considerable extent by the underground drainage from the upper part of the basin. This underground drainage water when it passes Harpenden contains about 11 of chlorine per million of water; but as it continues to percolate through masses of chalk at a great distance from the surface, it may be assumed to gain chlorides from the small residue of common salt remaining in the rock; so that wells in the lower part of the basin should, on an average, contain water richer in chlorides than wells at the edge of the basin.

I confess that I am not in a position to prove that the well waters of the chalk basin become, on an average, more chlorinous as they approach the centre of the basin; to establish such a point a multitude of observations would be necessary. Nor can I affirm (also from want of evidence) that the waters of deep uncontaminated wells are generally more chlorinous than the waters of shallow wells in the same district, though there are facts which seem to indicate that this is the case in Harpenden. It is clear, however, that the theory proposed involves no improbability, as large deposits of common salt are found in some rock formations in England; and the enormous depth of the chalk, and its resistance to the quick passage of water, are certainly favourable to the supposed imperfect removal of the sea water which it once undoubtedly contained.

Direct evidence as to the presence of common salt in the chalk seems to be furnished by the general considerable excess of chlorides in uncontaminated well waters over the amount furnished by rain, and present in the waters of land drainage (p. 519). Still stronger evidence is supplied by the condition of the well waters in the chalk when this formation is covered by the London clay. The clay has of course prevented any percolation of rain from above; the washing of this chalk has therefore for many ages been confined to the slow passage through it of water from the upper part of the basin, already containing chlorides. Under these circumstances we find a well water extremely rich in chlorides. Frankland found, as a mean of 13 well waters, 150·2 parts of chlorine per million of water. This richness in chlorides occurs in wells now far removed from the sea. Thus, three wells at Harrow gave a mean of 162·9 of chlorine per million of water. Prestwich, in his "Water-bearing Strata of London," 1851, p. 220, after discussing the conditions of the chalk beneath the London clay, concludes that the chlorine present most probably belongs to common salt originally present in the rock.

It would be of considerable interest to ascertain, if possible, what is the proportion of nitrates and chlorides in uncontaminated spring and well waters, collected from permeable strata, representing the cultivated districts of England; the proportion of nitrates in such waters should, if no nitrates have been lost by reduction in the subsoil, fairly represent the average loss which land suffers by drainage. The figures in the following table are taken from Frankland's analyses of unpolluted spring and deep well waters, given in the Sixth Report of the Rivers' Commission. Of the waters analysed from each formation, one-half of the samples, containing the largest proportion of chlorine, have been rejected, and the mean composition of the remainder taken; by proceeding in this way all instances of considerable previous sewage contamination are eliminated.

TABLE XIII.—*Nitrogen as Nitrates, and Chlorine, in the Purer Spring and Deep Well Waters from various Formations* (Frankland).

	Number of analyses.	Nitrogen as nitrates per million.	Chlorine per million.	Nitrogen per 100 of chlorine.
Devonian	13	3·7	20·1	18·4
New red sandstone	21	4·4	17·1	25·7
Oolite	19	2·8	12·3	22·8
Greensand (springs)	9	3·4	18·1	18·8
Chalk	47	4·2	16·5	25·4
Average of all	109	3·8	16·5	23·0

There is a considerable uniformity in the quantity of nitrates present in these waters, excepting the waters yielded by the springs in the oolite, which contain a distinctly smaller proportion of nitrates.

We have already seen that the minimum amount of nitrogen as nitrates in the pure underground water at Harpenden is 4·4 per million, corresponding to a loss of 1 lb. of nitrogen per acre for each inch of drainage. The mean proportion of nitrogen as nitrates shown by the analyses just quoted is 3·8 per million, this would correspond to a loss of 0·86 lb. per inch of drainage. If we assume for England, excluding the extreme western counties, an average annual drainage of 8 inches, we have 6·9 lbs. as the average annual loss of nitrogen per acre.

The amount of chlorine in the spring and well waters of the different formations is seen to be generally considerably above the Harpenden minimum of 11 per million, and still further above the amount (8 per million) calculated from the proportion found in the rain and drainage waters at Rothamsted. It is much to be regretted that, although rain water is systematically collected at a multitude of stations over the whole of England, the chlorine it contains has been rigorously determined only at Cirencester and Rothamsted. With the information at present at command, we must conclude that the chlorine in the rain is insufficient to account for that in the well waters, and that most probably a somewhat considerable part is derived from sea salt remaining in the rocks.

The only published results I am aware of respecting the composition of well waters at different seasons of the year are the monthly analyses made by Dr. E. Frankland of the chalk well waters supplied respectively by the West Kent Water Company, and by the Colne Valley Water Company, and published in the Annual Reports of the Local Government Board. The samples analysed are obtained from the mains of these Companies, and represent therefore in each case the mixed water of all the wells in work. The following table shows the average monthly contents of chlorine, and nitric nitrogen, in each of these series of well waters:—

TABLE XIV.—*The average Monthly Proportion of Chlorine, and Nitrogen as Nitrates, in the Chalk Well Waters supplied by the West Kent and Colne Valley Companies* (Frankland).

	West Kent well water, average 10 years, 1876–85.		Colne Valley well water, average 9 years, 1877–85.	
	Chlorine per million.	Nitrogen as nitrates per million.	Chlorine per million.	Nitrogen as nitrates per million.
November......	25·4	4·56	15·8	3·36
December......	25·1	4·63	15·8	3·52
January........	24·9	4·53	15·2	3·64
February.......	24·8	4·69	15·2	3·74
March.........	24·5	4·44	15·6	3·89
April..........	23·9	4·22	15·5	3·69
May...........	24·8	4·37	15·8	3·52
June	25·4	4·47	15·7	3·62
July...........	25·5	4·68	15·7	3·59
August	24 7	4·41	15·6	3·49
September......	24·6	4·43	15·8	3·48
October........	25·2	4·52	15·5	3·45
Mean........	21·9	4·50	15·6	3·58

The published determinations of chlorine and nitric acid are somewhat rough, and not very suitable for displaying small alterations in composition; fractions of a part per million of chlorine are seldom given.

In wells from which such enormous quantities of water are pumped we should expect to find the influence of the autumn and winter drainage from the surrounding soil practically extinguished by the far larger proportion of water brought up from the reservoir in the chalk; the water would thus exhibit a constant contents of nitrates, as well as chlorides, throughout the year. The chlorine in both the West Kent, and Colne Valley Companies' water, exhibits very little variation. The chlorine of the West Kent water shows perhaps a slight diminution in the early months of the year, when the water level would be rising in the wells. The low figure for April is, however, largely due to a single analysis; omitting this, the average of the month for nine years is 24·3. There is also a slight indication of a minimum of chlorine during January and February in the Colne Valley water. The nitrates in the Kent water show a tendency to a minimum in April (nitric nitrogen for nine years 4·35 per million), but there is no smooth progression in the figures. In the Colne Valley well water, on the other hand, the nitrates show a small but very regular alteration in amount; the minimum is in November, and the maximum in March. The figure for May seems a little too low (omitting one very low result, the mean is 3·75); the progression is else quite smooth. After the extremely wet winter of 1882–83, the rise of nitrates in the Colne water was very remarkable, the nitric nitrogen in February, March, and April being respectively 5·65, 5·48, and 5·27 per million. The seasonal change of nitrates in the Colne Valley wells appears therefore to be in the same direction as observed in the pure wells at Harpenden.

SUMMARY OF CHIEF FACTS.

1. The proportion of chlorine in the rain at Rothamsted, average of 9 years, is 2 per million. At Cirencester, average of nearly 16 years, it is 3·25 per million.

2. The proportion of ammonia in rain at Rothamsted, average of 5 years, is equal to 0·35 of nitrogen per million. The total combined nitrogen in the rain at Rothamsted is apparently not more than 0·67 per million.

3. The proportion of sulphuric acid in rain at Rothamsted, calculated as sulphuric anhydride. average of 5 years, is 2·52 per million.

4. At Rothamsted, with an average rainfall of 31 inches during 16 years, 14 inches have percolated through 5 feet of a bare clay soil

containing flints, and 17 inches have evaporated. The drainage is most active from October to February; in these 5 months 9½ inches have percolated, while in the remaining 7 months the percolation has been 4½ inches.

5. The quantity of chlorine in the water percolating through 5 feet of bare soil has been the same as that in the rain falling on the surface, but the proportion in the drainage water is nearly double that in the rain, becoming 3·9 per million (average of 9 years), in consequence of loss of water by evaporation.

6. The quantity of combined nitrogen in the drainage from 5 feet of bare soil has been, on an average of 9 years, about 9 times that supplied by the rain. The greater part of this nitrogen is in the form of nitrates, produced by the oxidation of the organic matter in the soil.

7. The proportion of nitrogen as nitrates in the drainage water from 5 feet of bare soil has been, on an average of 9 years, 10·7 per million. The production of nitrates occurs chiefly in the summer months. In the drainage from a bare shallow soil, the first considerable drainage which occurs after summer will contain the maximum proportion of nitrates, and the minimum will be reached in March. From a deep, unfissured soil, the drainage water will be of uniform composition, but varying greatly in amount throughout the year. From a bare soil 20 inches deep, the maximum discharge of nitrates is on an average in October; from a soil 60 inches deep, in November.

8. When land is covered by vegetation evaporation is increased; summer drainage almost entirely ceases, and the main winter drainage commences in November rather than in October.

9. Owing to the greater evaporation, the proportion of chlorine in the drainage from cropped land may be increased. The chlorine in the drainage water from the unmanured wheat land at Rothamsted is, on an average of 8 years, 6 per million. In the drainage from wheat land receiving much farmyard manure it is 7·3 per million.

10. Nitrates, being assimilated by plants, are generally almost entirely absent in the drainage from land bearing an actively growing crop. In the Rothamsted wheat field the drainage from the unmanured plot is usually free from nitrates from June till August. In the whole year the proportion of nitrogen as nitrates (average of 8 years) has been 3·4 per million in the drainage from this plot, and 5·8 per million where farmyard manure has been applied.

11. The amounts of chlorides and nitrates found in the drainage waters of the wheat field are probably below the true average, the years of observation having been generally years of excessive rainfall.

12. The average drainage from land under cereal crops will generally contain more nitrates than the drainage from the unmanured

wheat land at Rothamsted. The drainage from land carrying root crops will contain less nitrates than that from land bearing cereals; land in pasture will yield still less. The average amount of nitrogen as nitrates in the drainage waters of the district supplying the Harpenden wells, is shown by the composition of the uncontaminated well waters to be 4·4 per million.

13. With the amount of chlorine present in the Rothamsted rain, the average drainage from the cultivated land of the district can hardly contain more than 8 per million of chlorine.

14. The deep wells in the chalk at Harpenden derive their main supply from an underground flow of water, shown by the gradient of the water level to proceed from north-west to south-east. Each well receives besides a certain amount of local drainage.

15. To be able to detect the presence of oxidised sewage from the occurrence of an excess of chlorides and nitrates, we must first know what is the normal proportion of chlorides and nitrates in the uncontaminated water of the district.

16. The proportion of chlorine in the purest wells at Harpenden is about 11 per million of water. In such well waters the amount of chlorine does not sensibly vary throughout the year.

17. Well waters suffering little from sewage contamination will contain after long dry weather no more than the minimum proportion of chlorine.

18. Wells with much sewage in the surrounding soil may show the commencement of a rise in chlorides one or two months after active autumn drainage has commenced, and two months before the water level in the well begins to rise. Wells little liable to contamination show a rise in chlorides later in the season. Some wells escape contamination altogether in seasons when the local drainage fails to reach a considerable amount. A large rainfall in any month does not affect the chlorides in the well water before the following month. The maximum of chlorides in contaminated waters occurs after the end of the drainage season, usually in March or April. The minimum of chlorides is usually in September or October.

19. When the soil has been long contaminated by sewage, but all fresh contamination has ceased for many years, the chlorides in the well water may be considerably above the minimum proper to pure water, and yet remain nearly unaltered through the drainage season.

20. The minimum proportion of nitrogen as nitrates in the purest well waters of Harpenden is 4·4 per million. In an entirely uncontaminated well the proportion of nitrates may rise somewhat during the drainage season, if there is local percolation from a nitrifying soil.

21. In contaminated well waters the proportion of nitrates and chlorides increases during the early months of the drainage season at

a pretty equal rate. If active drainage continues for three months, a great increase in the proportion of nitrates usually takes place; and this relative excess of nitrates is maintained for some months after the period of maximum impurity is passed.

22. In a minority of the contaminated wells, while both chlorides and nitrates increase during the drainage season, there is no sensible alteration in their relation to each other. In these cases the impurity possibly enters the well at a lower level.

23. With a *normally distributed rainfall* the drainage season is from October to February, or with a smaller rainfall from November to February. The rise of the water level in the wells commences in January, and continues till March or April. The minimum contents of chlorides and nitrates in contaminated well waters is in October, the commencement of a rise in November. The maximum of chlorides in March or April, the maximum of nitrates in April.

24. The proportion of nitrates to chlorides in different well waters varies considerably. The sewage of a poorly-fed population yields a high proportion of chlorides to nitrates. Stable sewage furnishes apparently a high proportion of nitrates to chlorides. The old sewage contamination of deep wells is generally more or less chlorinous, chlorides being more permanent than nitrates.

25. The well waters of Harpenden contain the nitrifying organism in small proportion; it is probably derived from surface soil which has fallen in.

26. In the pure well water the sulphuric acid is scarcely in larger proportion than in the rain: a considerable part of the sulphuric acid in the rain has thus been retained by soil or plant.

27. In the contaminated waters the quantity of silica is not increased, and the quantity of carbonates but little increased. Lime is considerably increased, and magnesia still more. Sulphates are very largely increased.

28. On comparing the low proportion of chlorine found in the pure chalk waters of Harpenden, near the edge of the London basin, with the amount found in other chalk waters, and especially with the chalk waters beneath the London clay; and considering further the proportion of chlorides which can possibly be contributed by rain; it appears highly probable that a portion of the chlorides in chalk water, and probably in the water of other strata, is derived from a residue of sea salt remaining in the rock.

29. Numerous analyses made by Frankland of uncontaminated spring and deep well waters from various permeable formations in England, confirm the general idea obtained from the analysis of the Rothamsted drainage waters as to the average proportion of nitrates present in the drainage from cultivated land. The results of those

analyses point to 3·8 per million as a probable average proportion of nitrogen as nitrates in drainage water. The average loss of nitrogen to the soil by drainage is thus about 0 86 lb. per inch of drainage, or probably 7 lbs. per acre per annum.

XLIX.—*Constitution of Glycosine.*

By Francis R. Japp, F.R.S., and E. Cleminshaw, M.A.

Debus showed (*Phil. Trans.*, **148**, 209) that glyoxal reacts with ammonia according to the two equations—

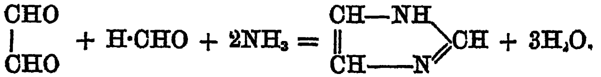
$$\text{I.}\ldots\ldots\quad \underset{\text{Glyoxal.}}{3C_2H_2O_2} + 4NH_3 = \underset{\text{Glycosine.}}{N_4(C_2H_2)^{iv}_3} + 6H_2O.$$

$$\text{II.}\ldots\ldots\quad \underset{\text{Glyoxal.}}{2C_2H_2O_2} + 2NH_3 = \underset{\text{Glyoxaline.}}{C_3H_4N_2} + \underset{\text{Formic acid.}}{CH_2O_2} + 2H_2O.$$

Radziszewski (*Ber.*, **15**, 1495) has suggested that the second of these reactions occurs in two stages. In the first stage 1 mol. of glyoxal is hydrolysed, yielding formaldehyde and formic acid; in the second, the formaldehyde reacts with another mol. of glyoxal and 2 mols. of ammonia, eliminating water and forming glyoxaline :—

$$(a.)\ C_2H_2O_2 + H_2O = CH_2O + CH_2O_2.$$
$$(b.)\ C_2H_2O_2 + CH_2O + 2NH_3 = C_3H_4N_2 + 3H_2O.$$

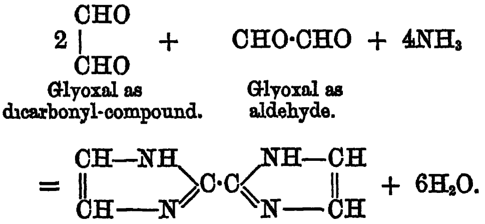
If this second stage is interpreted by the light of the condensations of dicarbonyl-compounds with aldehydes and ammonia studied by one of us (compare Equation II of the general reactions of this class, Trans., 1884, 672), the reaction would be expressed thus :—



Glyoxaline.

This is the formula for glyoxaline which was proposed by one of us (*Ber.*, **15**, 2419; see also Trans., 1883, 17). It is in keeping with the reactions of the compound, and has found general acceptance.

It occurred to us that the first of Debus's reactions—that in which glycosine is formed—might in like manner be interpreted as belonging to the class of dicarbonyl-aldehyde-ammonia condensations. Glyoxal is, from one point of view, a dicarbonyl-compound, and from another a dialdehyde. It would, therefore, only be necessary to assume that, of the 3 mols. of glyoxal taking part in the reaction, one has the function exercised by the aldehyde in such condensations, whilst the other two act as dicarbonyl-compounds. On this assumption, the reaction would occur according to the same general equation as the formation of glyoxaline from glyoxal formaldehyde and ammonia above referred to, save that in the present case, as the aldehyde is a dialdehyde, the molecular proportions of the other reacting substances are doubled:—

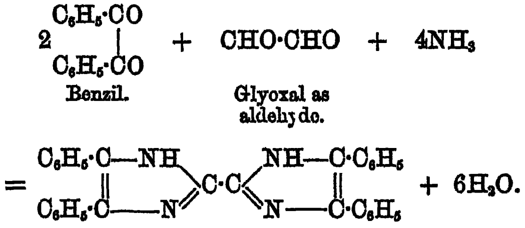


$$2\begin{matrix}CHO\\|\\CHO\end{matrix} + CHO{\cdot}CHO + 4NH_3 = \ldots + 6H_2O.$$

Glycosine.

The glyoxal molecule of aldehyde function reappears as an oxalic acid residue in the formula of glycosine; the two glyoxal molecules of dicarbonyl function reappear in the form of two unsaturated groups —CH : CH— (comp. Trans., 1884, 673). In this respect the reaction would belong to the numerous class involving mutual oxidation and reduction between similar molecules, to which class the aldehydes furnish the largest contingent.

If the foregoing view is correct, it should be possible to substitute, in the foregoing reaction, for the two glyoxal molecules of dicarbonyl function, two diketone molecules containing the group CO·CO. Thus, by the action of ammonia on a mixture of benzil and glyoxal, a *tetraphenylglycosine* should be formed:—



$$2\begin{matrix}C_6H_5{\cdot}CO\\|\\C_6H_5{\cdot}CO\end{matrix} + CHO{\cdot}CHO + 4NH_3 = \ldots + 6H_2O.$$

Tetraphenylglycosine.

The glyoxal was prepared by De Forcrand's method by the oxidation of paraldehyde with nitric acid, not purifying the glyoxal, however, but employing the syrupy mass obtained by evaporating the product of oxidation. The syrupy substance from 50 grams of paraldehyde was dissolved, together with 20 grams of benzil, in sufficient alcohol to keep the whole in solution at a temperature of about 40°, and the warm liquid was saturated with gaseous ammonia. After standing for 12 hours, the crystalline deposit was separated by filtration and warmed with dilute hydrochloric acid, which removed some ordinary glycosine. The alcoholic filtrate yielded, on concentration, a further deposit, which was treated in the same way. The substance insoluble in dilute hydrochloric acid was dissolved in boiling alcohol, and on cooling separated in tufts of very slender, felted needles, which, by repeated recrystallisation, were obtained pure white. The yield was very small. Analysis of the substance dried at 120° gave figures agreeing with the formula of tetraphenylglycosine, $C_{30}H_{22}N_4$:—

	Substance.	CO_2.	H_2O.
I	0·1679	0·5048	0·0815
II	0·1668	0·5033	0·0774

III. 0·1200 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18° and under 468·1 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 18·2° and under 399·6 mm. pressure.

	Calculated for $C_{30}H_{22}N_4$.		Found.		
			I.	II.	III.
C_{30}.....	360	82·19	82·00	82·28	—
H_{22}	22	5·02	5·39	5·16	—
N_4......	56	12·79	—	—	12·68
	438	100·00			

Tetraphenylglycosine is fairly soluble in hot, sparingly soluble in cold alcohol; readily soluble in glacial acetic acid. The solutions have a strong blue fluorescence. The crystals from alcohol have the formula $C_{30}H_{22}N_4,C_2H_6O$, but part with their alcohol over sulphuric acid, or when heated to 100°. Concentrated sulphuric acid dissolves it in the cold with a splendid green fluorescence. The dry substance becomes very electric when rubbed. Exposed to daylight it turns pink. The melting point, which lies above 300°, was not determined. Warming with alcoholic hydrochloric acid converts it into a hydrochloride, which forms strongly-refracting, yellow needles, differing in form from those of the base; but on drying the salt parts with a portion of its acid, and gave varying figures on analysis.

Debus regards as the most probable constitution of glycosine that of a tertiary amine formulated on the quadruple ammonia-type (see reaction I). The formula above suggested differs from this in containing two imido-groups. In order to prove the presence of two displaceable hydrogen-atoms, we have studied the action of benzyl chloride on glycosine.

Glycosine, prepared from glyoxal and ammonia,* was heated with an excess of benzyl chloride to the boiling point of the latter, until the whole formed a clear liquid, an operation requiring some time. The product was boiled with very dilute hydrochloric acid, which extracted the hydrochloride of a base. The base was precipitated with ammonia and purified by repeated recrystallisation from hot alcohol in which, unlike glycosine, it is very readily soluble. The crystals, which are only fully deposited after long standing, form colourless, transparent, oblique plates, sometimes grouped in rosettes, melting, with previous softening, at 145°—a melting point which is possibly somewhat too low, as the quantity of substance was insufficient for further recrystallisation. It is readily soluble in benzene, sparingly soluble in light petroleum. Analyses, in which we were obliged to content ourselves with a very small quantity of substance, gave figures agreeing fairly with the formula of a *dibenzylglycosine*, $C_6H_4N_2(N{\cdot}C_7H_7)_2$:—

I. 0·1118 gram gave 0·3105 gram CO_2 and 0·0589 gram H_2O.

II. 0·0671 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 13·5° and under 590·7 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. dry nitrogen at 13·5° and under 543 mm. pressure.

	Calculated for $C_6H_4N_2(N{\cdot}C_7H_7)_2$.		Found.
C_{20}	240	76·43	75·74
H_{18}	18	5·73	5·84
N_4	56	17·84	18·35
	314	100·00	99·93

The values found for carbon and nitrogen would suggest that the substance was contaminated with a small quantity of a monobenzyl-derivative.

The quantity at our disposal barely sufficed for analysis, so that we were unable to examine the salts of this base. Its existence proves the presence in glycosine of two displaceable hydrogen-atoms attached to nitrogen.

---

* We also tried Pinner's method of preparing glycosine from trichlorolactic acid and ammonia (*Ber.*, 17, 2000), but found the yield small and the substance difficult to purify.

In conclusion, we will communicate some observations relating to glycosine itself, but not bearing directly on the question of its constitution.

We find that glycosine can be recrystallised from boiling alcohol. It is only very sparingly soluble, but by employing a large bulk of liquid it is obtained in tufts of long white lustrous needles.

In his original memoir (*loc. cit.*), Debus gives a full analysis of the diacid platinichloride of glycosine, $C_6H_6N_4,H_2PtCl_6$; but, as regards the free base, he only publishes a nitrogen determination, stating that the carbon and hydrogen determination was lost, and that want of material prevented him from repeating the combustion. Kekulé (*Lehrbuch*, 2, 23) suggests that possibly glycosine and glyoxaline have the same composition, and are perhaps related to one another like hydrobenzamide and amarine. It therefore appeared to us of importance to make a combustion of glycosine, especially as the only combustions of it that appear to have been made—those by Pinner (*Ber.*, 17, 2000)—give the carbon 1·5 per cent. too low, and would, therefore, so far as this element is concerned, agree better with the formula of an isomeride of glyoxaline than with the accepted formula of glycosine. We employed for analysis the substance purified as above by recrystallisation from alcohol:—

0·1402 gram gave 0·2748 gram CO_2 and 0·0582 gram H_2O.

	Calculated for $C_6H_6N_4$.		Found.
C_6..........	72	53·73	53·45
H_6..........	6	4·48	4·61
N_4..........	56	41·79	—
	134	100·00	

We have also examined the platinichlorides of glycosine. By following the directions given by Debus we obtained the diacid salt, $C_6H_6N_4,H_2PtCl_6$, and confirmed its composition by a platinum determination. We have also obtained a monacid salt, $(C_6H_6N_4)_2,H_2PtCl_6$, the existence of which was suspected by Debus, and a tetracid salt, $C_6H_6N_4,(H_2PtCl_6)_2$.

The *monacid platinichloride* was obtained by adding a very dilute solution of platinic chloride to an excess of a solution of glycosine hydrochloride. It formed a pale buff-coloured precipitate which was homogeneous under the microscope, and consisted of hair-like crystals:—

0·0956 gram, previously dried in the steam-oven, gave on ignition 0·0268 gram platinum.

	Calculated for $(C_6H_6N_4)_2,H_2PtCl_6$.*	Found.
Pt in 100 parts........	28·71	28·03

The *tetracid platinichloride* is, of the three salts, that which is most readily prepared in a pure state. Excess of platinic chloride was added to a solution of glycosine hydrochloride, and the liquid was heated until the precipitate which was at first formed redissolved. On cooling, the tetracid salt separated in deep-yellow crystals, which were washed with dilute hydrochloric acid and then dried. The air-dried salt did not lose weight even at 120°.

0·1622 gram gave on ignition 0·0667 gram platinum.

	Calculated for $C_6H_6N_4,(H_2PtCl_6)_2$.	Found.
Pt in 100 parts........	40 82	41·12

It should be mentioned that a suggestion regarding the constitution of glycosine, similar to that here developed, has been thrown out by Wallach. He says (*Ber.*, **16**, 545, footnote) :—"Glycosine probably stands in the same relation to glyoxaline as dioxalethyline to oxalethyline." It is to be remarked, however, that dioxalethyline appears to be derived from an isomeride of glycosine in which the two glyoxaline complexes are united at a different point.

Normal School of Science,
South Kensington.

L.—*Diphenylglyoxaline and Methyldiphenylglyoxaline.*

By Francis R. Japp, F.R.S.

I received from Mr. W. Palmor Wynne about 3 grams of a crystalline base which he had obtained in very small quantity, together with imabenzil, benzilimide, and benzilam, by dissolving benzil in warm "methylated spirit" and saturating the solution with ammonia. The base remained in the last mother-liquors. It had been separated into several fractions, the purest having a pale pink colour and melting at 218°, whilst the less pure portions were dark-coloured and melted at 220—224°.

As the quantity was so small, I first attempted to prepare more of this base, and thinking that it might be a hitherto unobserved product of the action of alcoholic ammonia on benzil, substituted absolute alcohol for the methylated spirit of Mr. Wynne's experiment; but the only basic substance obtained was methyldiphenylglyoxaline (m. p. 235°), showing that the alcohol in question contained aldehyde. Before using the alcohol, therefore, it was boiled for several hours with caustic potash, to destroy aldehyde, and then distilled; but even then it yielded a trace of methyldiphenylglyoxaline, showing that the aldehyde had not been entirely removed. Mr. Wynne's base was not formed, and must therefore have owed its origin to some impurity in the methylated spirit employed.

---

* Pt = 194·5.

The experiment was then repeated, using methylated spirit; but again only methyldiphenylglyoxaline was obtained. The particular sample of methylated spirit employed by Mr. Wynne was unfortunately not available.

As the impurity in question was doubtless introduced into the methylated spirit with the crude wood spirit, I dissolved 50 grams of benzil in a large volume (about 4 litres) of commercial methyl alcohol, added a quantity of strong aqueous ammonia, and digested the whole on the water-bath for several hours. The methyl alcohol was then driven off, and the residue extracted with hot, very dilute hydrochloric acid. Ammonia precipitated from the hydrochloric acid solution a considerable quantity of a solid base, which was recrystallised from alcohol until colourless, when it melted constantly at 227°. The crystals from alcohol are of two forms: from hot alcohol the substance separates on cooling in long, oblique crystals (monosymmetric), which, on standing in the cold solution for some days, gradually redissolve, whilst lustrous short crystals (also monosymmetric, but not referable to the same parameters) are deposited; the latter form also separates from the cold alcoholic solution by spontaneous evaporation. Neither form contains alcohol of crystallisation; but the crystals from the hot solution, when heated to 120°, become opaque, without change of weight, being probably converted into aggregates of crystals of the second form. Analysis led to the formula $C_{15}H_{12}N_2$:—

	Substance.	CO_2.	H_2O
I	0·1018	0·3041	0 0509
II	0·1106	0·3303	0·0552

III. 0 0883 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 13·5°, and under 530·2 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 13·5° and under 504·2 mm. pressure.

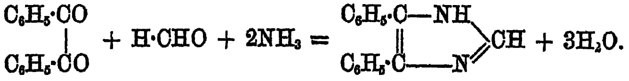
	Calculated for $C_{15}H_{12}N_2$.		Found.		
			I.	II.	III.
C_{15}	180	81·82	81·47	81·45	—
H_{12}	12	5·46	5·57	5·55	—
N_2	28	12·72	—	—	12·72
	220	100·00			

The *platinichloride* was obtained as a pale-yellow, amorphous precipitate, speedily changing into microscopic, flat needles, when platinic chloride was added to a solution of the hydrochloride of the base. The air-dried salt did not lose weight even at 120°.

0·1026 gram gave on ignition 0·0234 gram platinum.

	Calculated for $(C_{15}H_{12}N_2)_2,H_2PtCl_6$.	Found.
Pt in 100 parts........	22·90	22 81

The formula $C_{15}H_{12}N_2$ is that of a *diphenylglyoxaline*, which would be formed from benzil, formaldehyde, and ammonia according to the equation—



$$\begin{array}{l} C_6H_5{\cdot}CO \\ \quad\;| \\ C_6H_5{\cdot}CO \end{array} + H{\cdot}CHO + 2NH_3 = \begin{array}{l} C_6H_5{\cdot}C\text{—}NH \\ \qquad\| \qquad\quad > CH \\ C_6H_5{\cdot}C\text{——}N \end{array} + 3H_2O.$$

Diphenylglyoxaline.

In order to ascertain whether this compound, which had not hitherto been obtained, really was formed in this way, an alcoholic solution of benzil and formaldehyde (the latter prepared by Loew's method, by passing a mixture of methyl alcohol vapour and air over heated copper spirals) was warmed with ammonia. It was found that diphenylglyoxaline, identical in every respect with the foregoing base, could thus be prepared in any desired quantity.

I am indebted to Mr. L. Fletcher for the following description of the crystals of this compound:—

"Diphenylglyoxaline is dimorphous, the crystals obtained on cooling of a hot alcoholic solution being distinct from those deposited on spontaneous evaporation of the solution.

"A. *Crystals from Alcoholic Solution on Spontaneous Evaporation.*

"SYSTEM.—Monosymmetric.

"ELEMENTS.—$a : b : c :: 1{\cdot}227 : 1 : 1{\cdot}027$; $\eta = 121° 17'$.

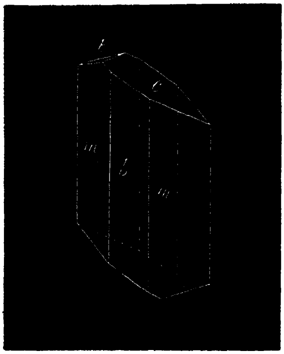
Or, $101{\cdot}100 = 32° 13'$; $111{\cdot}010 = 61° 18'$; $101{\cdot}001 = 26° 30'$.

"FORMS OBSERVED.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $t\{\bar{1}01\}$, $g\{011\}$.

"The development is illustrated in Fig. 1. The faces of the form $\{100\}$ are either absent or very small.

"The narrow faces of the form $\{011\}$ are not shown in the figure.

FIG. 1.



"The following measurements were obtained from five crystals—

Angles.	Observed	Calculated.
bm..........	43° 29′—43° 40′	43° 38′
$m\bar{m}_1$.........	92 43—92 45	92 44
mm_1.........	87 8—87 20	87 16
ct	51 14—51 42	51 41
cq	41 3 —	41 17
cm..........	69 2 —	69 0

"B. *Diphenylglyoxaline, Crystallised from Hot Alcohol.*

"SYSTEM.—Monosymmetric.

"ELEMENTS.—$a : b : c :: 1·394 : 1 : 1·269$; $\eta = 120° 44'$.

Or, $101·100 = 31° 10'$; $111·010 = 56° 43'$; $101·001 = 28° 6'$.

"FORMS OBSERVED.—$a\{100\}$, $c\{001\}$, $d\{\bar{1}02\}$, $t\{\bar{1}01\}$, $e\{\bar{1}22\}$, $f\{\bar{3}22\}$.

FIG 2.

"The development is illustrated in Fig. 2. The crystals are tabular through the extension of the faces of the form {100}, and are elongated parallel to the axis of symmetry: the narrow faces of the form {$\bar{1}$01} are not shown in the figure. There are easy cleavages parallel to the faces of both {001} and {100}.

"The following measurements were obtained from three crystals:—

Angles.	Observed.			Calculated.
ac	59° 14′,	59° 16′,	59° 18′	59° 16′
cd	27 6	27 7	27 10	27 1
dt	28 30	28 32		28 38
tā	65 4	65 6		65 5
ae	87 55	87 55		87 42
ef	33 42	33 53		33 54
fā	58 15	58 19		58 24
de	51 35	51 44	51 45	51 42
ee_1	76 39			76 36"

The crystals of diphenylglyoxaline, deposited from *cold* alcohol, closely resembled those of Mr. Wynne's base; but the difference in the melting points (227° and 218°) made it somewhat improbable that the two compounds were identical, especially as the effect of purification appeared to be to lower still further the melting point of Mr. Wynne's base. As the attempts to prepare a fresh supply of this base had thus proved unsuccessful, I set to work to purify the small quantity at my disposal, with a view to analysing it, and for this purpose dissolved the less pure fractions in dilute hydrochloric acid, intending to recrystallise the hydrochloride. It was immediately evident, however, either that the substance was a mixture, or that the hydrochloride crystallised in two forms. The hot solution of the hydrochloride, on cooling, deposited first a granular crystallisation, appearing under the lens as minute plates; afterwards tufts of fine silky needles began to separate, ultimately filling the entire liquid. The purest specimen of the base, in spite of its homogeneous appearance, behaved in a similar manner when dissolved in hydrochloric acid, except that the proportion of needle-shaped crystals was much smaller. These tufts of needles exactly resembled, both in appearance and in their manner of starting from the surface of the liquid, the hydrochloride of methyldiphenylglyoxaline, a substance which, as the foregoing experiment with methylated spirit, benzil, and ammonia showed, was very likely to be present. Advantage was therefore taken of the property which the needle-shaped crystallisation of this hydrochloride possesses of not separating from solutions from which air is excluded (Trans., 1886, 466), and the hydrochloride of Mr. Wynne's base was allowed to crystallise in corked test-tubes, into which the solution was poured while still hot. As soon as the separation of granular crystals was complete, the liquid with the crystals was filtered very rapidly through a platinum cone, and the crystals washed with water. Almost immediately a separation of needle-shaped crystals commenced in the filtrate, and in a few minutes the whole had solidified to a mass of these needles. These were separated by filtration, and the base liberated by ammonia and crystallised from alcohol, from which it separated in the characteristic forms of methyldiphenylglyoxaline, melting, like this base, at 235°. The whole of the methyldiphenylglyoxaline was not, however, removed from the substance in this one operation: beyond a certain concentration methyldiphenylglyoxaline hydrochloride, when allowed to crystallise in closed vessels, deposits granular crystals (Trans., 1886, 466), indistinguishable from those above described. In order to obtain the hydrochloride of the new base pure the crystallisation in closed vessels had to be repeated several times. From the various filtrates, after the needle-shaped crystals had been allowed to separate by exposure to the air, a further quantity of the new hydrochloride could be obtained, always mixed, however, with more or less of the needles. The test of purity, in every case, was to dissolve the new hydrochloride in a small quantity of water and allow it to evaporate spontaneously to dryness. If the whole crystallisation consisted of minute plates, the salt was taken as pure; if tufts of needles also appeared, the recrystallisation in closed vessels was repeated.

The new base, liberated from the purified hydrochloride, was three times recrystallised from alcohol. It was now colourless, and melted at 217—218°. The quantity was much diminished, since, apart from unavoidable loss in purification, about one-third of the original substance had been removed as methyldiphenylglyoxaline.

Analysis gave figures intermediate between those required for diphenylglyoxaline and methyldiphenylglyoxaline, or agreeing with the formula of a molecular combination of these two bases:—

I. 0·1281 gram gave 0·3842 CO_2 and 0·0689 H_2O.

II. 0·1105 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 19·5° and under 408·8 mm. pressure. After absorption of the nitric oxide there remained 22·63 c.c. of dry nitrogen at 20° and under 377·1 mm. pressure.

	Calculated for $C_{15}H_{12}N_2,C_{16}H_{14}N_2$.		Found.
C_{31}	372	81·93	81·80
H_{26}	26	5·73	5·98
N_4..........	56	12·34	12·40
	454	100·00	100·18

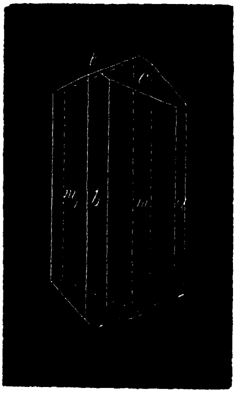
In order to ascertain whether this substance really was a molecular compound of this description, a mixture of diphenylglyoxaline and methyldiphenylglyoxaline, in equal molecular proportions, was dissolved in hydrochloric acid, and, after evaporating to dryness to expel the excess of acid, which otherwise interferes with the crystallisation, was redissolved in water and allowed to crystallise. The entire substance, even when the solution was allowed to evaporate spontaneously to dryness, was deposited in minute plates, exactly resembling the granular crystallisation of the hydrochloride of Mr. Wynne's base, none of the characteristic needles of methyldiphenylglyoxaline hydrochloride showing themselves. The mixed base was then liberated by ammonia and dissolved in alcohol, which deposited it in crystals indistinguishable from those of Mr. Wynne's base and, like these, melting at 217—218°. I have to thank Mr. Fletcher for finally establishing the identity by crystallographical measurements. He writes as follows:—

"*Base from 'Methylated Spirit,' Benzil, and Ammonia.*

"The crystals are identical in their crystallographic characters with those of the mixed base diphenylglyoxaline + methyldiphenylglyoxaline. Melting point 217—218°.

"The first crystals measured were pink; those received later were colourless.

FIG. 3.



"SYSTEM.—Monosymmetric.

"ELEMENTS.—$a : b : c :: 1{\cdot}212 : 1 : 1{\cdot}076$; $\eta = 120° \; 30'$.

Or, $101{\cdot}100 = 31° \; 42'$; $111{\cdot}010 = 60° \; 31'$; $101{\cdot}001 = 27° \; 48'$.

"FORMS OBSERVED.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $t\{\bar{1}01\}$, $u\{\bar{2}01\}$.

"The development is illustrated in Fig. 3. The faces of the form

{100} are either absent or very small on the synthetic crystals, as on those of diphenylglyoxaline deposited by spontaneous evaporation (p. 560), with which latter those of this double base are isomorphous, the angles in the prism-zone being virtually identical, but the angle *ct* differing by 2° 37′ in the two substances. It may be added that the angle *bm* in the prism-zone of the isomorphous crystals is almost identical with the angle 001·012 in one of the principal zones of the crystals of methyldiphenylglyoxaline (Trans., 1886, 465); the angle *bm* of the mixed base is 43° 45′, the angle *bm* of diphenylglyoxaline (A) is 43° 38′, whilst the angle 001—012 of methyldiphenylglyoxaline is 43° 58′. It was only on the synthetic crystals that the small triangular faces of the form {$\bar{2}01$} were observed. There is an easy cleavage parallel to the basal pinacoid {001}. One of the pink crystals was twinned, the twin-plane and composition-plane being (001).

"The following measurements were obtained from seven crystals:—

Angles.	Observed limits.	Best angles.	Calculated.
bm	41° 38′—47° 46′	—	43° 45′
$m\bar{m}_1$	92 8—93 23	—	92 30
ma	45 4—49 39	46° 16′	46 15
ac	57 13—59 13	59 0	59 30
ct........	52 49—56 27	54 15	54 18
tu	30 53—32 59	31 56	31 59
$u\bar{c}$	93 45—95 11	—	93 43
$t\bar{a}$........	67 0—71 30	67 19	66 12

"The variation of the angles is due to the curvature and striation of the faces."

The specimen of methylated spirit employed by Mr. Wynne therefore contained both acetaldehyde and formaldehyde, the latter of course introduced along with the wood spirit. The elaborate process of purification to which I had subjected the hydrochloride of the base merely had the effect of removing the *excess* of methyldiphenylglyoxaline hydrochloride. Beyond the point at which the two salts crystallise together, no further separation was possible by the method employed. Whether this point exactly corresponds with the combination in equimolecular proportions I am unable to affirm with certainty; but the results both of analysis and of the synthetic preparation of the mixed base point that way.

I have to thank my late assistant, Mr. Cosmo Innes Burton, B.Sc., for the care with which he has made the analyses given in this paper.

Normal School of Science,
South Kensington.

LI.—*On the Atomic Weight of Gold.*

By T. E. Thorpe, F.R.S., and A. P. Laurie, B.A.

Although gold is not usually regarded by chemists as one of the "rare" elements, it is remarkable that few atomic weights have been more imperfectly determined than that of this metal. This may be partly due to the circumstance that gold and its compounds have hitherto played a comparatively unimportant part as chemical reagents, and that the value of its atomic weight enters but seldom into chemical calculations. An additional reason may be found in the experimental difficulties with which such a determination is surrounded, owing to the unstable character of gold compounds in general. It is of course desirable that this, like every other stoïchiometrical constant, should be known with the greatest attainable precision in view of the far wider question than that of mere chemical equivalence with which the chemical philosophy of to-day deals. In the special case of gold, there is the further reason that the position of this metal in the system of the chemical elements, as determined by Mendeléeff's law, would seem to require a distinctly higher value for the atomic weight than is usually assigned to it. For these reasons, therefore, we were induced to undertake the revision of the atomic weight of gold, which forms the subject of the present communication.

Shortly after the publication by Dalton of his first table of atomic weights, attempts were made independently by Proust and Oberkampf in 1806 (*Gehlen's Journ.*, 1, 487) to determine the relation of gold to oxygen from the analysis of gold monoxide. Similar experiments were also made by Dalton, but the numbers obtained by all those observers were, as might be expected, not very concordant. Indeed, in the "New System of Chemical Philosophy," Dalton remarks "that the weight of an atom of gold is not easily ascertained because of the uncertainty in the proportions of the elements forming the compounds into which it enters. It is probably not less than 140 nor more than 200 times the weight of an atom of hydrogen." ("A New System of Chemical Philosophy," Part II, p. 250.)

The first approximately accurate determination of the atomic weight of gold was made by Berzelius in 1813 (*Kgl. Vetensk. Acad. Handl.*, 1813, p. 185; details taken from Sebelieu's "*Beiträge zur Geschichte der Atomgewichte*"). A neutral solution of auric chloride was digested for several days with a weighed quantity of mercury, in amount equal to about half that of the gold present, until the whole of the mercury was apparently dissolved. The precipitated gold was collected and weighed and afterwards strongly heated to expel the small quantity of mercury which invariably amalgamated with it; the volatilised mercury being collected and its weight subtracted from that originally taken. On the basis of Sefström's determination of the ratio between oxygen and mercury, Berzelius found from the two experiments which he made that Au = 1242·05 and 1249·65 (O = 100). From the relation $Au_2 : O_3$ = 100 : 12·040, Berzelius concluded that the mean value of Au = 1246. Taking H = 1, this value gives for Au 198·8. If Hg = 199·6, the two experiments give respectively Au = 196·0 and 197·3.

Pelletier (*Ann. Chim. Phys.*, **15**, 5), who first prepared aurous iodide, attempted to determine the atomic weight of gold by heating that salt and weighing the residue, which he regarded as pure gold. From the relation 100 gold : 51·515 iodine, he found the value of Au = 235 6. This abnormally high value doubtless arises from the instability of aurous iodide: the salt cannot be dried without loss of iodine, and decomposes even on exposure to light.

Javal (*Ann. Chim. Phys.*, **17**, 337), by heating auric oxide, Au_2O_3, prepared by adding baryta-water to a solution of auric chloride, obtained the relation $Au_2 : O_3$ = 100 : 11·909, whence Au = 201·0. Even higher values were given by Figuier (*Ann. Chim. Phys.*, **19**) from the analyses of the chloro-aurate of sodium. The gold was separated by means of sulphuretted hydrogen and the sodium chloride in the filtrate recovered by evaporation, the total chlorine in the double salt being determined in a separate portion by precipitation with silver. No numerical details of the analysis are given. The percentage composition of the salt is stated as 69·3 $AuCl_3$, 14·1NaCl, and 16·6 H_2O, whence Figuier deduces the value Au = 248·6. But from the relation NaCl : $AuCl_3$ = 14·1 : 69·3, the real value to be deduced from Figuier's numbers is 168.

In 1844, Berzelius (*Berz. Jahr.*, **25**, 41) again determined the atomic weight of gold by reducing chloro-aurate of potassium in hydrogen, weighing the residue, treating the mass with water, and weighing the gold. As these experiments have afforded the results upon which the usually accepted value for Au is based, it may be advisable to give the numerical details of the estimations.

The numbers are as follows:—

	Double salt taken.	Residue.	Potassium chloride.	Gold.
	grams.	grams.	grams.	grams.
I	4·1445	2·9775	0 8185	2·159
II	2·2495	1·61625	0·44425	1·172
III	5·1300	3·6360	1·01375	2·67225
IV............	3·4130	2·45125	0·6740	1·77725
V	4·19975	3·01975	0·8295	2·1880
	—	—	3·7800	9·9685

From the relation KCl : Au = 3·78 : 9·9685 we find that Au = 196·2 (H = 1).

In 1850, Levol (*Ann. Chim. Phys.* [3], **30**, 59) sought to determine the atomic weight of gold by dissolving a known weight of the metal in aqua regia and expelling the nitric acid from the chloride by repeated evaporation with hydrochloric acid, and reducing the aqueous solution by means of sulphur dioxide.

$$2AuCl_3 + 3SO_2 + 6H_2O = Au_2 + 3SO_4H_2 + 6HCl.$$

The sulphuric acid in the filtrate was then estimated as barium sulphate. As the result of two experiments, Levol found that 1 gram of gold was equivalent in the above equation to 1·782 grams of barium sulphate, whence he deduced the value Au = 195·9. Taking Stas's numbers for the molecular weight of $BaSO_4$, the value becomes 195·5.

Julius Thomsen found that hydrogen bromo-aurate,

$$AuBr_3,HBr,5H_2O,$$

contained 32·11 per cent. of gold and 52·00 per cent. of bromine, from which he concludes that Au is probably about 197 (*J. pr. Chem.*, 1876, **13**, 345).

It must be obvious that much of the discrepancy between the results of the foregoing observations can only be due to the very unstable nature of the gold compounds employed. On the other hand, some of the quantitative methods are bad in principle, and even with the most careful manipulation would be quite incapable of affording accurate values. The best methods would seem to be those of Figuier, and more especially of Berzelius; but, on reflection, it appeared to us unlikely that a mere repetition of the Swedish chemist's experiments, even if made with all the resources of modern quantitative analysis, would furnish us with more trustworthy numbers. A careful consideration of the properties of such gold compounds as seemed suitable induced us to hope that the *bromo-aurate of potassium* might prove to be well adapted to our purpose. A number of specimens of this salt were therefore prepared by various methods and repeatedly crystallised. It was found that the ratio of the auric bromide to the potassium bromide in the double salt was perfectly constant even after five and six crystallisations. The salt, too, is easily decomposed, and at temperatures far below that at which potassium bromide volatilises. We doubt, however, whether the salt can be wholly dehydrated by heating, without loss of bromine; hence, as will be seen below, our method of analysis was so devised as to obviate the necessity of drying the salt. We found that the mixture of finely divided gold and potassium bromide could be weighed in a covered porcelain crucible without risk of error from hygroscopic moisture, and there was no difficulty in separating the last traces of the alkaline bromide by treatment with hot water. Samples of gold so washed, dried at 140—150°, and weighed, showed no loss of weight after being heated for two or three hours to the highest temperature of a muffle furnace.

These preliminary points being satisfactorily settled, we arranged the following plan of work:—An unweighed quantity of the bromo-aurate (say from 12 to 15 grams) was placed in a large porcelain crucible, previously weighed against a precisely similar crucible, and then heated for some hours at a temperature gradually increasing to about 160°, after which it was still more strongly heated over a small Bunsen flame. The auric bromide readily parts with its bromine, and with due care there is no risk of loss by decrepitation or by the potassium salt being mechanically carried away with the escaping bromine. The tare is of course heated in precisely the same way, both crucibles, in fact, being treated from first to last in the same manner. The decomposed salt was then weighed, and the salt again heated in order to ascertain that the weight was constant.

By treatment with hot water, the potassium bromide was separated from the gold, the solution being drawn over by the method of reverse filtration which one of us has already employed in the course of the experiments which served to fix the atomic weight of titanium (*Chem. Soc. Journ.*, Trans., 1885, **47**, 108). The washed gold was then heated in a muffle in a porcelain crucible, and weighed against a similar crucible similarly treated and used as a tare. The ratio of the weight of the gold to that of the potassium bromide afforded one value for the atomic weight of gold.

A second value for Au is got by comparing the weight of the washed gold with that of the silver which would be required to precipitate the whole of the bromine in the solution of potassium bromide.

And lastly, a third value is found by comparing the weight of the washed gold with the weight of the silver bromide formed in the second series of observations.

Two balances were made use of in the course of the determinations, a long-beamed instrument by Oertling, and a short-beamed instrument by Wolters, for the loan of which we are indebted to Dr. Hodgkinson. The weights were of gilded brass by Standinger; they were the set already used by one of us in the determination of the atomic weight of titanium, and had been previously compared amongst themselves and their errors determined by the method of vibrations. The weighings were made by the method of vibrations, the balances being placed in a room set apart for the purpose.

The corrections employed for reduction to a standard atmosphere were as follows:—

Per gram of gold = − 0·00010
" potassium bromide = + 0·00031
" silver bromide = + 0·00006
" silver = − 0·00002

The method adopted for the preparation of the silver was identical with that already described in the memoir "On the Atomic Weight of Titanium" (*loc. cit.*). It consisted in reducing purified silver chloride by means of hot solutions of pure soda and milk-sugar in silver vessels, treating the reduced silver with ammonia, washing with distilled water, and fusing on a support of "brasqued" lamp-black.

The fusion was made at the lowest possible temperature, and as the metal cooled it was surrounded by a faintly luminous flame in order to diminish the chance of the occlusion of oxygen. There can, however, be little doubt that the error due to this cause is much less than the observations of Dumas would seem to imply. Mallet, in the course of his experiments on the determination of the atomic weight of aluminium, found only about 30 c.c. of oxygen per kilo. of silver, and more recently van der Plaats (Beiblätter, *Ann. Phys. Chem.*, **10**, 579) observed that silver prepared by Stas's method lost no weight on being heated in a vacuum or in a stream of hydrogen or carbon monoxide.

Professor Roberts-Austen, who has in many ways shown a very practical interest in our work, was good enough to compare the silver thus prepared with the standard trial plate used in connection with the coinage. He reported that after very careful assays, two from each of the four sample buttons sent, it appeared safe to conclude that the silver in question had a standard fineness of 999·5, the trial plate being taken as 1000·0.

The method of preparing the pure silver for this plate is described in the "Report of the Deputy Master of the Royal Mint" for 1873.

It was identical with that recommended by Stas, depending upon the reduction of an ammoniacal solution of a silver salt by means of ammoniacal cuprous sulphite, and the purity of the metal was tested by distillation in a lime crucible by the aid of the oxyhydrogen blowpipe. It is the practice in the Mint to regard the fineness of the trial plate as 999·9 compared with silver prepared by Stas himself. On the basis of these comparisons, we have assumed that 1 gram of the metal employed by us contained 0·9994 gram of real silver.

The gold was prepared from old assay cornets, by dissolving them in nitrohydrochloric acid, evaporating to get rid of excess of nitric acid, diluting with a large quantity of distilled water, and allowing it to stand for some weeks to remove traces of silver. It was then precipitated by well-washed sulphurous acid gas, and the spongy precipitate repeatedly boiled with distilled water till every trace of chlorine was removed. The cornets used were those obtained from the check assays, and consisted originally of pure gold.

The gold used, after preparation, was assayed against the trial plate at the Mint. Taking the trial plate as 1000, this gold is 999·93. The trial plate itself is not so pure as it was before rolling, being reduced from 1000 before rolling to 999·95 after rolling. Consequently the purity of the gold used as compared with the original trial plate is 999·88.

Of this trial plate, Professor Roberts-Austen states in the Mint Report, that he has never been able to obtain from any source gold in a greater state of purity. In its preparation, special care was taken to remove traces of platinum* by treating the dissolved gold with alcohol and chloride of potassium.

The pure potassium bromide was prepared from the potassium bromide made according to the Pharmacopœia. It was found to be absolutely free from iodine, and was treated to remove any possible traces of chlorine by dissolving in water and adding sufficient absolute alcohol to produce a slight precipitation of the KBr. The solution was then filtered and evaporated, and the bromide allowed to crystallise out. These crystals, drained of mother-liquor, were dissolved and again partially precipitated with alcohol. The crystals obtained from the second filtration were drained, dried, and heated over a Bunsen in a porcelain crucible.

The bromine was prepared from the purified potassium bromide by distilling it with pure chromic acid and pure sulphuric acid. The bromine thus obtained was carefully redistilled. It still contained a little water, but this was immaterial.

---

* The effect of any trace of platinum, if present, would be to lower the atomic weight. The double bromide of potassium and platinum is a sparingly soluble salt. Platinum present in the gold used for assaying, is revealed at once by the appearance and behaviour of the button of alloy obtained in cupelling, even though only present in minute quantities. No indications of its presence have been observed in assaying this gold at the Mint.

In order to prepare the potassium bromo-aurate, a weighed quantity of gold with its equivalent of potassium bromide was placed in a stoppered bottle; a large excess of bromine and a considerable quantity of water were next added, and the stopper inserted and tied down.

At first, the reaction between the gold and the bromine was sufficiently vigorous to heat the contents of the bottle; afterwards it proceeded more slowly, and was completed in about 36 hours. When the gold had completely dissolved, the solution was evaporated down, the double salt allowed to crystallise out, and the crystals drained thoroughly from mother-liquor. After the third crystallisation, the well-drained crystals were considered sufficiently pure for the atomic weight determination.

Series I. Au : KBr.

The potassium bromo-aurate, contained in a large porcelain crucible of known weight, was gently heated, at first in an air-bath and then over the rose of a Bunsen burner until bromine was no longer evolved. As soon as the weight was constant, the mass was treated with hot water and the solution of potassium bromide was drawn over by reverse filtration into a bottle which could be closed by a well-fitting stopper. The gold was left as a loosely coherent cake of a brownish-yellow colour. It was readily washed, and there was no difficulty in removing the last traces of the potassium bromide. The gold was then dried in the air-bath and heated to bright redness in a muffle.

The results of the several estimations are seen in Table I.

TABLE I.

Wt of Au + KBr.	Wt. of Au.	Wt of KBr.	At wt Au (II
9 92441	6·19001	3·73440	196 88
7 64672	4·76957	2·87715	196 90
6·63872	4·14050	2·49822	196 86
5 77784	3·60314	2·17440	196 85
5·89941	3·67963	2·21978	196·89
7 33952	4·57757	2·76105	196·86
8·60480	5·36659	3·23821	196·85
8·27939	5·16406	3·11533	196 89

Series II. Au : Ag.

The weight of the potassium bromide obtained in the several estimations being known, an amount of silver—slightly less than that required for its total decomposition—was weighed out into a $\frac{1}{4}$-litre flask and dissolved in the minimum quantity of nitric acid of sp. gr. 1 21. The solution was effected at the lowest possible temperature, so as to exclude the possibility of loss by portions being mechanically carried away in the gaseous products. The solution was then heated to expel the last traces of the lower oxides of nitrogen, diluted with water, and transferred to the bottle containing the potassium bromide. The liquid, made turbid by suspended silver bromide, was violently shaken until clear, and the last traces of the bromide were precipitated by the addition of a solution of silver nitrate of known strength (1 c.c. = 0·0010818 gram silver). The operation was carried out in substantially the same manner as that described by Stas, the room being illuminated by red light only. The results of this series of experiments are seen in Table II.

Table II.

Weight of gold.	Weight of silver.	At. wt. Au (H = 1).
6·19001	3·38451	196·90
4·76957	2·60896	196·82
4·18266	2·28830	196·78
4·14050	2·26415	196·88
3·60344	1·97147	196·78
3·67963	2·01292	196·81
4·57757	2·50334	196·87
5·36659	2·93608	196·78
5·16406	2·82401	196·87

Series III. Au : AgBr.

The precipitated silver bromide obtained in the preceding series of experiments was then transferred to a weighed porcelain crucible, the solution of the potassium nitrate being removed by reverse filtration in the manner already described (*loc. cit.*). The crucible containing the well-washed bromide, together with the small platinum rose and disc of filter-paper, was heated at first to about 90—100° and afterwards at about 160° until its weight was constant. In some of the experiments, the bromide was fused after a constant weight had been found at 160° and again weighed, but no alteration sufficiently large to affect the second decimal place in the atomic weight was ever perceived. Silver bromide can be thoroughly dried by sufficiently prolonged heating at 160°.

The results of the several weighings are seen in Table III.

TABLE III.

Weight of gold.	Weight of silver bromide.	At. wt. Au (H = 1).
6·19001	5 89199	196 89
4·76957	4 54261	196·77
4 18266	3 98288	196 81
4·14050	3·94309	196 79
3·60344	3·43015	196 88
3 67963	3 50207	196·91
4·57757	4·35736	196 88
5 36659	5·11045	196·80

The total weight of the silver bromide obtained from the several determinations given in Series III is 34·76060 grams: it was formed from 19 96973 grams of metallic silver employed in the preceding series. Hence Ag : AgBr = 1 : 1·74072.

From Marignac's experiments (*Bibl. Univ. Genève*, **46**, 360) it would appear that—

Ag : AgBr .... 1 : 1·74077

Stas (*Nouv. Rech.*, p. 158, 1865) found the ratio—

Ag : AgBr .... 1 : 1·74081

The close accordance of our results with those of Stas and Marignac is at once a proof that the correction applied to the silver was perfectly valid, and that the silver bromide and hence the bromo-aurate from which it was derived was practically free from chlorine.

Calculation of the Results.

The value of Au has been calculated from each experiment in order to show the agreement among the various observations. Instead of simply taking the mean of the several results it is better to deduce the final results from the aggregate weights of the gold, potassium bromide, silver and silver bromide: in this way the influence of the large quantities employed is directly felt.

We take from Stas the following ratios of Ag, Br, K, O, and H:—

Ag	6 7449
Br	4 99634
K	2 44523
O	1
H	0·06265

On the basis of these numbers we may thus summarise the results of the various observations :—

Series I. (8 *Experiments*).

Au : KBr	37·49137 : 22·61944
„	1·65748 : 1
Au : O	12·3343
Au : H	196·876

Series II. (9 *Experiments*).

Au : Ag..................	41·67403 : 22·79374
„	1·82831 : 1
Au : O	12·3318
Au : H	196·837

Series III. (8 *Experiments*).

Au : AgBr................	36·50997 : 34·76060
„	1·05033 : 1
Au : O	12 3322
Au : H	196 842

On the assumption that these values have equal weight, the final value from the whole 25 experiments becomes—

	Au.	Diff. from mean.
Series I...........	196·876	+ 0·024
„ II...........	196·837	− 0·015
„ III...........	196·842	− 0·010
Mean	196·852	

Probable error of one series........	± 0·014
Probable error of result............	± 0·0082

A considerable proportion of the determinative work connected with this investigation had been accomplished, when there appeared in the *Ber. deut. chem. Ges.* for February, 1887, a paper by H. Gerhard Krüss on the same subject (**20**, 205). We had originally contemplated extending our observations so as to include a direct comparison of the atomic weights of gold and silver, and a determination of the ratio of gold to cyanogen in aurous cyanide. The results we had been able to obtain from the potassium bromo-aurate agreed so closely with those of Krüss that it seemed useless to prolong the inquiry. Krüss also made use of potassium bromo-aurate, but his method of treating the salt differed somewhat from that employed by us. Krüss assumed that the double salt could be obtained absolutely anhydrous by heating, without loss of bromine, and further that it was so slightly hygroscopic that it could be weighed without risk of absorbing moisture. As we had doubts on both these points, we so arranged our plan of work that it was unnecessary either to dry the double salt or to know its weight. The presence of moisture in the bromo-aurate in no degree affected the determination of the ratios upon which our values of Au depended. Krüss obtained four values for Au from his analysis of the bromo-aurate. A weighed quantity of the double salt was reduced, in some cases by heating in a current of hydrogen, and in others by treatment in aqueous solution with sulphurous acid. From the relation of the weight of the gold to (1) that of the double salt taken; (2) to the loss of weight in hydrogen; (3) to the total weight of bromine weighed as silver bromide and obtained as such by adding silver nitrate to the aqueous solution of the double salt after reduction with sulphurous acid; (4) to that of the potassium bromide obtained by dissolving out the potassium bromide after heating the double salt in hydrogen, Krüss obtained the following values:—

		Au (H = 1).
I. Au : KBr,Br_3	(9 experiments).....	196·741
II. Au : Br_4	(5 „).....	196·743
III. Au : Br_3	(4 „).....	196·619
IV. Au : KBr	(4 „).....	196·620

The results of I, II, and III would be affected by any moisture in the salt or by any loss of bromine in dehydrating. The values from IV are alone directly comparable with our own, as they may be regarded as obtained from unknown weights of the bromo-aurate. The weight of the potassium bromide in Krüss's observations was, however, determined after the evaporation of the aqueous solution of the salt, and not, as in our case, by subtracting the weight of the gold from that of the double salt after decomposition by heat. Hence any moisture left in the salt after evaporation would tend to lower the atomic weight of Au.

The lower value of Au obtained by Krüss from the analyses of the gold potassium bromide agrees, however, with the results of his analyses of a neutral solution of auric chloride prepared by decomposing by warm water, auro-auric chloride obtained by Thomsen's method, weighing the gold (after reduction with sulphurous acid), and the chlorine as silver chloride. From the relation Au : Cl_3, Krüss obtained Au = 196·594. This value would, of course, be affected by any free chlorine left in the double chloride after treating the finely divided metal with that gas. In Krüss's experiments, the occluded chlorine was removed by aspirating dry air over the product and then allowing it to stand over soda-lime for some time before decomposition with water.

From the results of all his observations, Krüss adopts 196·64 as the most probable value for Au—a difference of 0·21 from the mean value obtained by us.

We cannot conclude this communication without expressing our acknowledgments to Professor Roberts-Austen and to Messrs. Rigg and Bailey, of the Royal Mint, for the assistance they have rendered us throughout the course of this investigation.

LII.—*On the Atomic Weight of Silicon.*

By T. E. Thorpe, F.R.S., and J. W. Young, B.A.

All the values for the atomic weight of silicon which have been hitherto obtained are based upon the analysis of silicon tetrachloride, or rather upon the ratio of equivalent weights of silicon tetrachloride, silver, and silver chloride. Berzelius, it is true, sought to determine the atomic weight of this element by converting silicon into the dioxide, and also from analyses of barium silicofluoride, but the results were recognised by him as unsatisfactory, and were practically withdrawn.

In the appendix to Professor F. W. Clarke's "Recalculations of the Atomic Weights," published by the Smithsonian Institution, the atomic weight of silicon is marked as "very badly determined," and the statement is abundantly justified by the facts.

The value usually given in tables of atomic weights rests upon two not very concordant determinations of the ratio of silicon tetrachloride to silver made by Dumas on about a couple of grams of the liquid. When we consider the extraordinary part which silicon plays in the inorganic world, it seems remarkable that a physical constant of so much importance as its atomic weight should have been allowed to remain so long upon such a limited experimental basis.

The first analyses of the chloride undertaken with a view of determining the atomic weight of silicon were made in 1845 by Pelouze (*Compt. rend.*, 20, 1047) on a sample of the liquid prepared by Ebelmen. A known weight of silver dissolved in nitric acid was brought in contact with slightly more than the equivalent weight of silicon chloride, previously decomposed by water, and the excess of the chlorine precipitated by the addition of a silver solution of known strength. Only two determinations were made, and they gave respectively Si = 28·35 and 28·46 (H = 1).

In 1859, Dumas (*Ann. Chim. Phys.* [3], 55, 183) repeated Pelouze's observations, and in two experiments obtained Si = 27·95 and 28·11.

Schiel (*Annalen*, **120**, 94) in 1861 determined the relation of $SiCl_4$ to AgCl by decomposing silicon chloride by means of a slight excess of a dilute solution of ammonia, adding silver nitrate, and weighing the silver chloride. Two estimations were made. They gave respectively Si = 27·83 and 28·07. The aggregate weight of the silver chloride employed was less than 2 grams.

There is no question that of all the combinations of silicon the halogen compounds are the best adapted for determinations of its atomic weight, provided that suitable precautions are taken. Hence we have been led to seek for a more accurate value for Si by determining the relation of $SiBr_4$ to the SiO_2 formed on decomposing the tetrabromide by water. For this purpose, we prepared in the first place about half a kilogram of the tetrabromide by passing bromine vapour over a strongly heated mixture of pure silica and finely ground willow charcoal such as is used in the manufacture of gunpowder. The silica and charcoal were intimately mixed, made into a stiff paste with oil, rolled into balls, ignited in a closed crucible. and then loosely packed into a large and wide porcelain tube placed in a coke furnace. The product, which of course contained considerable quantities of free bromine, was rectified by distillation in an apparatus of which the various parts were connected together either by sealing or grinding. The liquid was then shaken with mercury, decanted, and placed in contact with sheet copper for some weeks, and again distilled in an atmosphere of dry nitrogen. The tetrabromide was absolutely clear and colourless, and boiled constantly at 153°. In order to collect portions for analysis without exposure to air, we adopted the same arrangement as that already employed by one of us in the course of the determination of the atomic weight of titanium (Trans., 1885, 108), and the general method of filling the bulbs was similar to that described in the communication referred to.

The bulb containing the weighed quantity of silicon bromide was brought into a well-stoppered bottle, together with about 10 times its weight of water, and after breaking the bulb with all the precautions described in the paper on the atomic weight of titanium, the turbid liquid was decanted into a tared crucible, and evaporated over a water-bath, an equal volume of water being evaporated under the same conditions in the tare. The thorough washing of the bottle and the fragments of glass remaining in it, and the evaporation of the liquid used, occupied about a week. At the end of that time, the crucibles were dried in an air-bath, which was gradually raised to 160°, after which they were ignited in a muffle to a bright red heat, allowed to cool, and weighed against each other with the same precautions to prevent dehydration which were adopted in the case of titanic oxide (*loc. cit.*).

The balances and weights employed were identical with those used in the determination of the atomic weight of gold (see preceding communication).

In weighing, the method of vibrations was invariably used, a zero reading being taken both before and after weighing in every case, and the value of a scale division for the particular load was determined by shifting the rider 0·4 or 0·6 milligram at the time.

The corrections for reduction to a standard atmosphere were—

Per gram of silicon tetrabromide....	+ 0·0003	gram.
„ „ dioxide	+ 0 00042	„

We have assumed with Lothar Meyer and Seubert that the most probable ratios for the atomic weights employed in our calculations are—

Br	4·99721
O..................	1
H	0·06265

The atomic weight of silicon [x] was calculated from the equation—

$$x + 319{\cdot}04 : x + 31{\cdot}92 :: \text{wt. } \textit{in vacuo} \text{ of } SiBr_4 : \text{wt. } \textit{in vacuo} \text{ of } SiO_2.$$

The following table contains the results of our experiments:—

Wt. of $SiBr_4$ *in vacuo*.	Wt. of SiO_2 *in vacuo*.	Ratio of Si : H.
9·63007 grams.	1·67070 grams.	28·347
12·36099 „	2·14318 „	28·303
12·98336 „	2·25244 „	28·317
9·02269 „	1·56542 „	28·352
15·38426 „	2·66518 „	28·243
9·74550 „	1·69020 „	28·325
6·19159 „	1·07536 „	28·429
9·51204 „	1·65065 „	28·366
10·69317 „	1·85555 „	28·364

The aggregate weight of silicon tetrabromide employed in the various experiments was 95·52367 grams: it yielded 16·56868 grams silicon dioxide. This corresponds to

$$Si = 28{\cdot}332,$$

which number we accordingly adopt as the most probable value for the atomic weight of silicon.

We made several attempts to determine the bromine in the aqueous solution of hydrobromic acid obtained by adding a weighed quantity of silicon tetrabromide to water, so as to obtain the ratio of $SiBr_4$ to Ag, and thus another value for Si, but the results were unsatisfactory owing to the difficulty of perceiving the end-point in the volumetric reaction. Volhard's method also, though easy of application, was not sufficiently accurate for our purpose. After a few experiments it seemed hopeless to expect that we should obtain numbers which would compare in point of precision with those which were furnished by our determinations of silica. It will be observed that our value more nearly approximates to that of Pelouze than to that of Dumas, which has hitherto been accepted as the most probable number.

LIII.—*Note on Substitution in the Benzene Nucleus.*

By Dr. H. F. Morley.

Dr. Armstrong has recently drawn renewed attention to the regularities that may be observed in the conversion of the mono-derivatives of benzene into di-derivatives. As may be seen from the tables that he gives (this vol., p. 259), when one atom of hydrogen in benzene has been displaced by CH_3, CH_2Cl, Cl, Br, I, OH, NH_2, NHAc, $CH_2{\cdot}CO_2H$, or $CH{:}CH{\cdot}CO_2H$, the resulting compound gives, when a second substitution takes place, a para- or an ortho-derivative; whereas when an atom of hydrogen in benzene has been displaced by one of the radicles NO_2, CN, CO_2H, COH, SO_3H, $SO_2{\cdot}C_6H_5$, or $CO{\cdot}CH_3$, a new element or radicle entering the benzene nucleus takes up a meta-position with regard to the radicle already present (see also Nölting, *Berichte*, 9, 1797). The radicles producing para- or ortho-derivatives are more basylous than those producing meta-derivatives; this will readily be admitted in the case of amidogen, methyl, and side-chains beginning with CH_2 or CH, but it might be disputed in the case of the halogens. The halogens are of course "chlorous," but they are less chlorous than nitroxyl, carbonyl, carboxyl, or sulphoxyl. This is apparent when we compare ethyl malonate, $EtO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OEt$, and nitro-ethane, $CH_3{\cdot}CH_2{\cdot}NO_2$, on the one hand, with methylene chloride, $Cl{\cdot}CH_2{\cdot}Cl$, and ethyl chloride, $CH_3{\cdot}CH_2Cl$, on the other, for the former yield sodium-derivatives,

$EtO{\cdot}CO{\cdot}CHNa{\cdot}CO{\cdot}OEt$, and $CH_3{\cdot}CHNa{\cdot}NO_2$, whilst the latter do not. It will be noticed that all the radicles under discussion are attached to benzene by a chlorous element (N, C, S, or a halogen), and that where this element stands alone (the halogens) or is attached also to one or more basylous elements (as in OH, NH_2, CH_3) the radicle induces para- or ortho-substitution, whilst radicles in which the chlorous "grouping" element is attached to other chlorous elements (as in NO_2, CO_2H, or SO_3H) induce meta-substitution. Accordingly we find that CCl_3 and $CHCl_2$ are capable of giving rise to meta-derivatives, whilst CH_2Cl resembles CH_3 in its characters, the two atoms of hydrogen preponderating over the single atom of chlorine. The formation of meta-nitro-benzylidene chloride by the nitration of benzylidene chloride can hardly be explained by the "molecular-addition" theory, which will shortly be referred to.

It appears, therefore, that the more basylous a radicle is, the less does it induce *meta*-substitution, but the view adopted by Dr. Armstrong, in a note which he read at a recent meeting of the Society, appears to take an exactly opposite view.

I drew attention to this at the time, but was assured by the author that this was not the case, as would be found on careful study of his paper. Accordingly I postponed further criticism until I could make myself thoroughly familiar with Dr. Armstrong's point of view. The result of this study has been to confirm my original objections, and as it appears very desirable that points of such theoretical importance should be fully discussed, I venture again to draw the attention of the Society to this matter.

Dr. Armstrong says (Proc., **2**, 44): "Having in my mind the fact that the 'basic' powers of nitrogen become enhanced by introduction of hydrocarbon radicles in place of hydrogen, it appeared not improbable that the behaviour of a compound such as dimethylaniline, for example, would not in all cases be strictly in accordance with the para-ortho law." This sentence seems to me to mean that the more basylous a radicle becomes, the less is its behaviour in accordance with the para-ortho law, a statement which is directly contrary to the views I have just been advocating. Whether dimethylaniline is or is not more basic than aniline is a question which does not affect the interpretation I have given to the sentence.*

In studying Dr. Armstrong's original paper, I believe I have found the explanation of the statement in question. The author does not consider that the chlorous or basylous character of the radicle has anything to do with the laws of substitution, but that *unsaturated* radicles, which can *combine directly* with a molecule of the reacting substance (HNO_3 or Br_2) produce meta-derivatives, whilst saturated radicles which cannot so combine produce para- or ortho-derivatives. In the latter case, it is assumed that molecular combination nevertheless takes place, this time, however, between the reacting substance and *one of the atoms of carbon in the benzene nucleus.*

---

* If a mixture of equivalent quantities of aniline and dimethylaniline be more than half neutralised with aqueous hydrogen chloride in the cold, the greater part of the uncombined base is dimethylaniline.

It is obvious that, if this view be accepted, such an unsaturated radicle as amidogen, which can of course combine with HNO_3, ought to produce a meta-derivative. Unfortunately for the theory in question, the chief product, when aniline is nitrated in presence of not too large an excess of sulphuric acid, is paranitraniline. In order to avert the conclusions that may naturally be drawn from this experiment, Dr. Armstrong draws attention to some experiments on the nitration of benzene-derivatives containing the radicles NMe_2 and NHEt, which, however, may receive a very different interpretation from that which he gives.

In order to prove that alkyl-amidogen groups give rise to meta-substitution products, Dr. Armstrong relies on the following facts:—

That dimethylaniline sulphate, diethylaniline sulphate, ethylaniline sulphate, and ethylparatoluidine sulphate all produce *meta*-nitro compounds when nitrated, whereas aniline, bromodimethylaniline, and paracetyltoluidine give rise to *para*- or *ortho*-nitro compounds, the terms *ortho*, *meta*, and *para* being applied to the position taken up by the nitroxyl relatively to amidogen or alkylamidogen.

In the discussion which followed the note in question, I remarked that the effects observed were not due so much to the character of the original substance as to the manner in which the nitration was performed. It has been shown by Nolting and Collin (*Berichte*, **17**, 261), that when aromatic bases are nitrated in presence of a *very* large excess of sulphuric acid, cooled with ice and salt, *meta*-nitro compounds are produced, and that the amount of meta-compound so obtained is increased by increasing the quantity and strength of the sulphuric acid used.

Thus paracetyltoluidine, when nitrated by means of fuming nitric acid, *in absence of sulphuric acid*, gives an *ortho*-nitro-derivative, and the same result follows if only 4 parts of sulphuric acid are mixed with it; if 10 parts of sulphuric acid are used, a mixture of *meta*- and *ortho*-nitro-derivatives is formed, and on increasing the amount of sulphuric acid the proportion of the *meta*-derivative formed rises at the expense of the *ortho*-derivative. Paratoluidine itself, when nitrated in presence of 10 parts of sulphuric acid, gives both *ortho*- and *meta*-nitro derivatives, but when 20 parts of sulphuric acid are used, the *meta*-derivative is the only one formed. This shows that the presence of Me or Et in the amidogen is in no sense necessary to the formation of meta-derivatives. Orthotoluidine and its acetyl-derivative, when nitrated without the use of sulphuric acid, produce *para*-nitro derivatives, but when 20 parts of sulphuric acid are used the *meta*-nitro derivatives are the only ones formed. The same remarks apply to metaxylidine and to parabromaniline. Indeed the only case which appears at all doubtful is that of aniline itself. Nölting and Collin state, however, that by using 50 parts of sulphuric acid they succeeded in greatly reducing the amount of paranitraniline formed, and a patent for preparing metanitraniline by projecting aniline nitrate into cold sulphuric acid has been taken out (*Berichte*, **18**, Ref., 203).

There is therefore no proof that alkylated amidogen has a greater tendency to produce meta-compounds than amidogen itself; in presence of a large excess of sulphuric acid, both produce meta-compounds; in the absence of sulphuric acid, neither produce meta-compounds.

The explanation of this phenomenon given by Hübner seems to me to be still tenable. We are dealing with sulphates. The group $N(SO_4H)H_3$ is more chlorous than NH_2, and hence gives rise to meta-derivatives. It remains to explain why the *quantity* of sulphuric acid can exert any influence on the result. I imagine that when but little sulphuric acid is present we have in the liquid not only molecules of the sulphate of the base but also free base, and that when nitric acid is added some of it attacks the base and some the sulphate, hence we get a mixed product; but by increasing the amount of sulphuric acid we can diminish the relative number of molecules of the free base until there are practically none left, and then we get a pure meta-derivative.

It is well known that aniline sulphate dissolved in water, when treated with bromine, gives a precipitate of tribromaniline, sulphuric acid remaining in solution; but I have observed that bromine is without action on aniline dissolved in cold strong sulphuric acid; even on raising the temperature, the greater part of the bromine is expelled in the free state. From this we may perhaps conclude that a solution of aniline sulphate contains free aniline which is precipitated by bromine, the equilibrium of the solution being thereby destroyed, more aniline being formed and precipitated, &c.

Be this as it may, the mechanism suggested by Dr. Armstrong to explain the formation of di-derivatives of benzene requires us to assume that when dimethylaniline is converted into paranitrodimethylaniline by nitration in acetic acid solution, the nitric acid begins by combining, not with the nitrogen, but with an atom of carbon in the benzene nucleus, an assumption which is surely in the very highest degree improbable.

LIV.—*An explanation of the laws which govern substitution in the case of benzenoid compounds.* (Second Notice.)

By HENRY E. ARMSTRONG.

IN the foregoing note Dr. Morley traverses the explanation which I recently put forward of the laws which govern substitution in the case of benzenoid compounds (this vol., pp. 258—268; Proceedings, March 17th, 1887, p. 44). The paper in question was written with no intention of treating the subject exhaustively, and much was left to be said on some future occasion when the results of experiments now being carried out were ripe for publication; my desire being to rekindle interest in a problem of very great importance which has become somewhat hidden from view by the extraordinary number of new facts discovered within recent years, and to attract attention to the study of the nature of the changes involved in the formation of substitution-derivatives. I perceive, however, that I have not made my meaning sufficiently clear, and Dr. Morley's criticisms are most welcome as indicating where further explanation is necessary.

Referring to my paper, Dr. Morley says: "Dr. Armstrong . . . does not consider that the chlorous or basylous character of the radicles has anything to do with the laws of substitution, but that *unsaturated radicles* which can *combine directly* with a molecule of the reacting substance produce meta-derivatives, whilst saturated radicles which cannot so combine produce para- or ortho-derivatives. In the latter case, it is assumed that molecular combination nevertheless takes place, this time, however, between the reacting substance and *one of the atoms of carbon in the benzene nucleus.* It is obvious that if this view be accepted, such an unsaturated radicle as amidogen, which can of course combine with HNO_3, ought to produce a meta-derivative." This reference by no means represents my views. I certainly am of opinion that the influence which the radicle exerts does not depend on its being basylous or chlorous: the similarity in the behaviour of compounds containing hydrocarbon radicles or amidogen on the one hand with those containing the halogens or hydroxyl is sufficient to prove this; the terms in question are to my mind of value chiefly as indicating the character of a substance which will enter into combination with such radicles, or to which they bear resemblance. I have never stated, however, "that unsaturated radicles which can combine directly with a molecule of the reacting substance produce meta-derivatives, while saturated radicles which cannot so combine produce para- or ortho-derivatives"; in fact, I do not regard even the radicles Cl, Br, I, or OH as saturated.

Still I confess that my paper contains several paragraphs which taken together almost justify Dr. Morley's statement. The reference on p. 265 to certain cases of isomeric change is sufficient to prove, however, that I did not mean to imply that in the formation of para- and ortho-derivatives the reacting molecule always combines with one of the atoms of carbon of the benzene nucleus; it should also be evident that only unsaturated radicles of a particular kind, not unsaturated radicles generally, were held by me to favour the production of meta-derivatives.

I have suggested that in the case of mono-derivatives of benzene which furnish the ortho- or para-di-derivative, it may be held that an additive compound is first formed by the union of the reacting molecule with the *carbon-atom* of the mono-derivative to which the radicle R′ is attached. The hydrogen-atom in benzene being, by hypothesis, saturated, the formation of additive compounds such as that of benzene with trinitrophenol, or with antimony trichloride, $Sb_3Cl_9 \cdot 2C_6H_6$ (Watson Smith), may be regarded, I imagine, as conclusive evidence that in the case of benzene itself combination may take place in the manner here supposed.

Now it is well known that the homologues of benzene are acted on by bromine—in fact, by reagents generally, far more readily than is benzene, the difference being more and more striking as the series is ascended. It is particularly remarkable that the introduction into so sluggish a hydrocarbon as benzene of radicles bearing so simple a relation to the *paraffins*—of radicles which might be expected to behave very much as paraffins do, should render the benzene residue so susceptible of attack; and that by association with a benzene residue, a paraffinoid radicle such as CH_3 should itself become so susceptible of attack, for example, by bromine under the influence of light. I venture to think that the difference arises from the greater readiness of the homologues of benzene to form additive compounds; and I regard their behaviour as conclusive evidence that they are less saturated compounds than benzene. It would seem indeed that the C_nH_{2n+1} radicle is not fully equivalent to the hydrogen-atom which it displaces in benzene; or that by its introduction the symmetrical distribution of the "affinities" is disturbed or modified (*ante*, p. 264). Whatever view be taken, the facts would seem to indicate that the point at which the radicle is attached becomes a locus of attraction. It is certainly open to question whether in the case of the benzenes any part of the attraction proceeds from the hydrocarbon radicle, or whether it proceeds solely from the carbon atom of benzene to which the radicle is attached: I hold it to be possible that the attraction results from their conjoint action; that CH_3 in a benzene is less saturated than CH_3 in a paraffin. But we have at present no means of solving such a problem, and as the C_nH_{2n+1} radicles are universally regarded as saturated, it appeared to me desirable to adopt as a working hypothesis the assumption that in the formation of (molecular) additive compounds from the benzenes, the added molecule becomes united with the carbon-atom to which the hydrocarbon radicle is attached.

The same argument applies to chloro-, bromo-, or iodo-derivatives of benzene; but it is to be noted that in the case of the halogen elements clear evidence is afforded by the production of double chlorides, &c., that these elements are not saturated when associated with other elements in equivalent proportions: we *must*, therefore, be prepared to admit that in haloid derivatives of hydrocarbons the halogen is more or less unsaturated. Schramm has stated (*Ber.*, **18**, 607) that if benzene and bromine be mixed in the proportions $C_6H_6 : Br_2$, at most about 50 per cent. of the benzene is converted into bromobenzene; the bromobenzene appears to form an additive compound with the remainder of the bromine, thus protecting the benzene. This observation may be held to indicate that the bromobenzene has the superior attraction for bromine, and that the influence of a halogen on benzene is in this respect of the same order as that of a C_nH_{2n+1} radicle. Whether the attraction is exerted by the carbon-atom only, or by both the carbon-atom and the halogen attached thereto, it is impossible to decide; and on this account again the hypothesis is perhaps preferable that the additive compound is formed in the manner already indicated. It is important however, to note that whereas by the introduction of C_nH_{2n+1} radicles into benzene the "reactivity" (*Einwirkungsfähigkeit*) of the compound is increased, the introduction of halogen would appear to produce the contrary effect; and to compare this with the fact that bromobenzene yields a large proportion of para-, and but little ortho-derivative, while toluene, for example, yields a large proportion of ortho-, together with the para-derivative. It may be that this difference is to be explained by simple dynamical considerations; but it is of interest as bearing on the question of the manner in which the para- and ortho-derivative originate. The conversion of an additive compound formed in accordance with our hypothesis into the ortho-di-derivative would, as already remarked (*ante*, p. 263), appear to follow as a matter of course; on the other hand, if the added molecule unite with the radicle, it is conceivable, and as I shall point out there is evidence to support the view, that an additive compound thus constituted may give rise to the para-di-derivative only. If it should prove possible to draw any such distinction between the modes in which ortho- and para-derivatives are generated, it would follow that in the case of bromobenzene the additive compound is formed almost exclusively by the union of the added molecule with the bromine, and that in the case of toluene the additive compound to a large extent results from the union of the new molecule with the carbon-atom with which the C_nH_{2n+1} radicle is associated. In the former case but little effect is produced by varying the conditions, the proportion of ortho-derivative being always small; but in the latter, much depends on the conditions, and it would be necessary to assume that isomeric additive compounds are formed in proportions which vary greatly according to circumstances.

The behaviour of amido- and hydroxy-derivatives, which is in many respects peculiar, deserves minute study from the above point of view, several highly suggestive observations having been recorded from which it may be inferred that the phenomena of substitution are less simple than is perhaps commonly supposed, and that isomeric change is by no means of infrequent occurrence in the formation of derivatives of amines and phenols. Thus acetanilide is converted by the action of hypochlorous acid into the compound $C_6H_5{\cdot}NCl{\cdot}C_2H_3O$, from which in a variety of ways the isomeric *para*chloracetanilide is readily obtained: for example, by heating it to about 170°, the melting point of parachloracetanilide; by the action of cold concentrated chlorhydric acid; or by warming it with alcohol (Bender, *Ber.*, **19**, 2272). The conversion of the nitrosamine, $C_6H_5{\cdot}NMe(NO)$, into paranitrosomethylaniline already referred to (*ante*, p. 265)* is a similar case. Piria's observation (*Annalen*, **78**, 31) that when nitronaphthalene is boiled with an alcoholic solution of ammonium sulphite, a mixture of the ammonium salt of thionaphthamic acid, $C_{10}H_7{\cdot}NH{\cdot}SO_3H$, and of naphthionic or *para*midonaphthalenesulphonic acid, $C_{10}H_6(NH_2){\cdot}SO_3H$, is produced, appears to place beyond doubt the possibility of the formation of an amidosulphonic acid from the isomeric compound in which SO_3H is associated with the nitrogen; and the formation of potassic phenol*para*sulphonate from potassic phenylic sulphate is an instance of a similar change in the case of a phenol.† These examples, although few, are perhaps numerous enough to justify the enquiry whether the formation of para-derivatives of primary or secondary amines and of phenols is not always preceded by that of an isomeric compound formed by the displacement of the aminic or hydroxylic hydrogen. Whether ortho-derivatives are formed in a similar manner remains to be ascertained; the conversion of sodic phenylic carbonate, $NaO{\cdot}CO{\cdot}OC_6H_5$, into sodic salicylate (Schmitt, *J. pr. Chem.*, 1885, **31**, 397) is the only instance of the production of an ortho-derivative of benzene by isomeric change which occurs to me. Claisen's recent observation (*Annalen*, **237**, 263) that the formation from an aldehyde and betanaphthol of the condensation product $R{\cdot}CH(C_{10}H_6{\cdot}OH)_2$, is preceded by that of the isomeric acetal, $R{\cdot}CH(O{\cdot}C_{10}H_7)_2$, is, however, probably also a case of "ortho-isomeric change."

---

* A slight correction in the paragraph in which this reference occurs may be here made · the words "For example," with which the sentence begins, should be put after the words "the observation that"

† It appears to me probable that the formation of azo-compounds from amines and phenols by the action of diazo-salts takes place in a similar manner, and that the conversion of the diazo-amido- into the amido-azo-compound is a case of direct isomeric change.

Undoubtedly much remains to be learnt regarding the mode of action more particularly of agents such as nitric and sulphuric acids. Thus we are unable at present to explain the formation of isomeric sulphonic acids, for example, from naphthalene, from phenol, and from betanaphthol. It is commonly held that the formation of either the α- or the β-sulphonic acid from naphthalene is a question of temperature, and that the conversion of the former into the latter on heating with sulphuric acid involves in the first place the formation from the α-acid of sulphuric acid and naphthalene, and the subsequent resulphonation of the latter. From experiments which Mr. Wynne and I have made, however, I much doubt whether under any conditions naphthalene can be directly converted into the β-sulphonic acid; and it appears probable that this acid is formed either by the conversion of the α-acid into a disulphonic acid—which then undergoes partial hydrolysis, or by sulphonation of a sulphate: there can be little doubt that its formation is dependent on the presence of sulphuric acid in excess. If betanaphthol be very carefully treated with sulphuric acid, it is converted into the sulphate $C_{10}H_7{\cdot}OSO_3H$, which—as Nietzki and I have shown—may be isolated; this sulphate is completely transformed into the isomeric sulphonic acid (Schaefer's modification) by heating it for a short time at 100°. But by submitting betanaphthol to the action of sulphuric acid at a temperature not exceeding 60—70°, an acid isomeric with the foregoing (Baeyer's modification) may be obtained; on raising the temperature to 100°, however, this acid is rapidly converted into Schaefer's modification. How is the formation of this second sulphonic acid to be explained; is the sulphate first formed, and does this undergo isomeric change into either the one or the other sulphonic acid, according to the temperature to which it is heated? I am inclined to believe rather that the sulphate yields only Schaefer's acid: in fact, that the production of this acid is dependent on the prior formation of the sulphate; and that Baeyer's modification results from the interaction of the sulphate and sulphuric acid. Betanaphthol is converted by treatment with a single molecular proportion of chlorosulphonic acid into betanaphthylsulphate; if the product be treated with a second molecular proportion of the acid, a disulphonic derivative is produced (*Ber.*, 1882, 200); from the manner in which this was formed, I was originally of opinion that it was a sulpho-sulphate, but by a more recent study of the reaction I have been led to think that it is a disulphonic acid derived on the one hand from Schaefer's and on the other from Baeyer's acid. The chief point of interest is the fact that, on boiling an aqueous solution of this disulphonic acid, hydrolysis takes place, and it is converted into Schaefer's monosulphonic acid. It would therefore seem probable that the sulphate which is the initial product is converted on further sulphonation into the sulphate of Baeyer's acid; that when SO_3HCl is used, this latter product spontaneously changes into disulphonic acid; but that when sulphuric acid is the sulphonating agent the sulpho-sulphate undergoes hydrolysis, yielding Baeyer's acid; and finally that when the temperature is raised, Baeyer's acid either undergoes direct conversion into Schaefer's acid, or is converted into sulpho-sulphate, which in turn undergoes isomeric change into the disulphonic acid, and this latter then suffers hydrolysis. These cases illustrate very clearly the complexity of the phenomena of substitution.

It remains for me to justify the reference in my brief note in the Proceedings to the probable behaviour of dimethylaniline to which Dr. Morley takes objection. The term "basic" was used to give expression to the idea—formed from a study of the ammonium-compounds—that the nitrogen in such a tertiary amine is in a more active, less saturated, condition than it is perhaps in aniline itself. It was impossible, as no aminic hydrogen was present, that the para-derivative should be formed by direct isomeric change in the manner above suggested; and it therefore appeared probable, as aniline sulphate was known to yield the meta-nitro-derivative in small quantity, that dimethylaniline sulphate would give a still larger proportion of meta-derivative, both because it was less likely to give the para-derivative, and because it would have a greater tendency to form an additive compound. Nolting and Collin's most interesting results (*Ber.*, 17, 261), to which Dr. Morley calls attention, appear to me to entirely support this view.

The aminic derivative which is converted by isomeric change into the para-derivative, being produced from the ammonium salt (when the agent is an acid): it is conceivable that, when owing to absence of aminic hydrogen such a derivative cannot be formed, the salt itself may undergo direct conversion into the para-derivative, especially in presence of a powerful dehydrating agent such as sulphuric acid.*

---

* The formation from tertiary amines and diazo-salts of substituted amido-azo-

Therefore the presence of a large quantity of sulphuric acid would favour the production of the meta-nitro-derivative by preventing the formation of nitrate, as has been observed to be the case. The additive compound which yields the meta-derivative is, I assume, in all probability formed by the union of the nitric acid with the sulphate, not with the amine. Many of Nolting and Collin's observations appear to afford direct confirmation of the above interpretation: thus in presence of 15—20 parts of sulphuric acid, paratoluidine gives only the meta-nitro-derivative; but paracetoluide, which undoubtedly would form a much less stable sulphate than paratoluidine, although more chlorous, does not give the meta-derivative as sole product, even when a much larger excess of acid is used. There is a similar difference between orthotoluidine and orthacetoluide. A low temperature would also give increased stability to the sulphate, and would therefore favour the production of the meta-compound. On the other hand, if acetic acid were used instead of sulphuric, the acetate being less stable, the nitrate would undoubtedly be formed and give rise to the para-derivative.

Dr. Morley's statement that "the group $N(SO_4H)H_3$ in aniline sulphate, &c., is more chlorous than NH_2, and hence gives rise to meta-derivatives," is but a phrase: it may be doubted whether the radicle $NH{\cdot}C_2H_3O$ in acetanilide is more chlorous than the radicle $NH_2{\cdot}SO_4H_2$ in aniline sulphate; and inasmuch as compounds containing the basic radicle NH_2 or allied groups, and those containing the chlorous radicles Cl, Br, &c., in most respects behave alike, it does not follow that the change from a less to a more chlorous radicle would have the marked effect which sulphuric acid has. No doubt every change in composition—every change in the distribution of the affinity—has its proper effect, however. A particularly instructive illustration is afforded by the behaviour of toluene as compared with that of its chlorinated derivatives: thus, toluene and benzyl chloride yield only a very small proportion of meta-nitro-derivative, but it would appear that the proportion of paranitro-derivative obtained from the latter at low temperatures is much larger than from the former (*Ber.*, **17**, 385, 1073; **19**, 137); benzalchloride and benzotrichloride, however, readily yield meta-nitro-derivatives.

Finally, there is one other fact to which attention may be called, viz., the formation of metabromobenzoic acid from silver benzoate by means of bromine: if, as is probable, the silver is initially displaced, a bromoxy-compound being formed which then undergoes isomeric change, this instance affords information of value with regard to the

---

compounds (Griess, *Ber.*, **10**, 525), in my opinion, affords conclusive evidence that the change may and does take place in this manner.

constitution of the additive compounds from which meta-derivatives are derived.

Whatever the ultimate value of the explanation advanced by me, regarded merely as a working hypothesis, it at least has the merit of indicating various directions in which it is important to advance experimental enquiry; and I am persuaded that the principle on which it is founded is of wide application.

City and Guilds of London Institute,
Central Institution.

LV.—*Researches on Silicon Compounds and their Derivatives.* II. *A New Chlorobromide of Silicon.*

By J. Emerson Reynolds, M.D., F.R.S., Professor of Chemistry, University of Dublin.

I have already pointed out that silicon tetrabromide is a more manageable reagent than the chloride for use with organic substances (Trans., 1887, 202). But the bromide does not appear to have been produced in quantity from the date of its discovery by Serullas in 1831 (*Ann. Chim. Phys.*, **47**, 87), until I obtained more than a kilogram of it by a slight modification of Serullas' process. In the course of the purification of this large quantity five years ago, I separated a liquid from which I have lately obtained the new chlorobromide of silicon described in this paper.

The crude tetrabromide was prepared by the action of the vapour derived from commercial bromine on a mixture of silica with carbon, heated in a good wind furnace. The best results were obtained when the mixture was most intimate, and this was secured by making a paste of gelatinous silica, the purest form of lampblack, and syrup of cane-sugar; this mass was formed into pellets, then dried and ignited.

The purification of the silicon bromide was carried out in the following way:—A current of dry hydrogen was led through the warmed liquid, in order to remove most of the free bromine; the residue was then shaken up with metallic mercury which completely decolorised the liquid, and the latter was then subjected to fractional distillation in a dry atmosphere. Out of 1·2 kilos. of liquid only a few drops passed over below 140°, but a considerable fraction was obtained between 140° and 144°, and another between 145° and 148°, after which the temperature rose rapidly to 153°. The last distillate consisted of nearly pure tetrabromide, which completely solidified to a beautiful crystalline mass at −12°. The fraction between 140° and 144° did not afford any crystals when kept for several hours below −14°; nor did the higher fraction either.

The liquid of lower boiling point* was then separated by repeated fractionation into a small quantity of a substance which boiled below 140°, a relatively large amount boiling between 140—141°, and some more tetrabromide.

The liquid boiling at 140—141° is colourless and fumes in the air like the tetrabromide. Its sp. gr. is 2·432; that of the tetrabromide being 2·82. When added to water, it is quickly decomposed, and affords a mixture of silicic, hydrobromic, and hydrochloric acids.

The following determinations were made with this compound:—

I. 4·5259 grams were added to water in a platinum dish; when decomposition was complete, the liquid was evaporated to dryness and the residue ignited; it was then moistened with ammonium hydrate and ignited again for half an hour. SiO_2 weighed 0·9211 gram = 9·57 per cent. of Si.

II. 3·4225 grams similarly treated gave 0·698 of SiO_2 = 9·59 of Si. Mean of the two experiments 9·58 of Si. The formula $SiClBr_3$ requires 9·35 per cent. of Si.

III. 2·8325 grams were added to water, and the liquid, when cold, was diluted to 500 c.c.

a. The weights of silver required to precipitate the chlorine and bromine in two separate quantities of 100 c.c. each were determined. The mean value found was 4·09146 grams of silver for the above weight of chlorobromide; consequently 100 parts = 144·4 of silver. The formula $SiClBr_3$ requires 142·13 of silver.

b. 200 c.c. were just neutralised by ammonium hydrate, the solution boiled for some time, then filtered to remove silica, and the filtrate precipitated by excess of silver nitrate. The mixed precipitate of AgBr and AgCl weighed 2·6746 grams, or 6·6865 for the total weight of chlorobromide taken; this corresponds to 235·1 for 100.

The percentage composition of the substance is:—

	$SiClBr_3$ requires.	Found.
Si	9·35	9·57
Cl	11·67	12·12
Br	78·98	78·53

---

[*] A similar fraction was separated from a quantity of crude tetrabromide made for me by Dr. Schuchardt.

The vapour-density of the compound by Meyer's method, and in aniline vapour, proved to be 10·43. Theory requires 10·47.

The liquid analysed is therefore *silicon chlorotribromide* containing traces of a body richer still in silicon and chlorine. Its chlorine has obviously been derived from the crude bromine used in the preparation of the tetrabromide. The chlorotribromide is, then, the chief product of the action of chlorine on the silica and carbon mixture in presence of a large excess of bromine.

By the isolation of the chlorotribromide we are now acquainted with a complete series of the compounds possible between silicon tetrachloride on the one hand and tetrabromide on the other. The chlorobromide $SiCl_3Br$ was obtained by Friedel and Ladenburg (*Ann. Chim. Phys.* [4], 27, 416) as the chief product of the action of bromine on silicon trichlorosulphydrate and on silicon chloroform; in the latter case, they also obtained the chlorobromide $SiCl_2Br_2$. The boiling points of the series of compounds are given in the following table:—

	B. p.
$SiCl_4$..................	59°
$SiCl_3Br$	80
$SiCl_2Br_2$................	100
$SiClBr_3$.................	141
$SiBr_4$..................	153

It would be of interest to compare the boiling points of the silicon haloïds with those of the corresponding carbon compounds; but the data for the latter are not all obtainable.

University Laboratory,
Trinity College, Dublin.

LVI.—*On the Thermal Phenomena of Neutralisation, and their bearing on the Nature of Solution and the Theory of Residual Affinity.*

By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College.

The thermal phenomena attending the heat of neutralisation of acids with alkalis supply us with one of the fundamental data of thermochemistry, and, even were they less remarkable in character, would be of sufficient importance to warrant a full investigation and discussion. No such investigation has, as far as I am aware, been made; and it has become all the more necessary that the results should now be examined, since they appear to be very generally misinterpreted, and have been used of late as arguments for theories which are directly opposed to their teaching; as an instance of which misinterpretation I may refer to Nicol's oft-repeated assertion that they prove his views as to the dissolution of a salt being a physical and not a chemical action (*Chem. News*, **54**, 53—192; Trans., 1887, 396; &c.).*

The explanation which I give of the thermal results of neutralisation is in substance identical with that briefly suggested by Armstrong in reply to Nicol's statements at the meeting of the British Association last year (*Chem. News*, **54**, 217), and depends on the recognition of the existence of residual affinity, a view which each of us has independently advocated (Pickering, *Proc. Chem. Soc.*, 1885, 122; Armstrong, *B. A. Report*, Aberdeen, 1885, Address to Sec. B; *Proc. Roy. Soc.*, 1886, 268).

When a metallic hydroxide in solution (*i.e.*, containing K, Na, Li, Tl, Ba, Sr, Ca and Mg) is neutralised by an acid, the heat evolved is independent of the nature of the metal. The evolution per atom of hydrogen displaced amounts to 13825 cal. in the case of hydrochloric acid, 13805 cal. with nitric acid, and 15583 cal. with sulphuric acid (Thomsen, *Thermochem. Untersuch.*, 1, 418). On the other hand, when a given base (sodium hydroxide) is neutralised by different acids, it is found that a large number of these yield results identical with those given by hydrochloric acid and nitric acid, namely, about 13800 cal. per hydrogen-atom displaced, notably so in the case of HBr, HI, $HClO_3$, $HBrO_3$, and HIO_3; but, on the other hand, there are a considerable number which yield lower results, and a few which give higher results, although of those investigated, hydrofluoric acid alone gives a higher value than sulphuric acid (15580 cal.).

---

* For an instance of a very gross misinterpretation of the results of neutralisation, see *Chem. News*, **55**, 144, 227.

With other dyad metals, the hydroxides of which are insoluble, the heat of neutralisation is lower than in the above cases, and different in each individual case, but it is found that they also yield identical results with both nitric and hydrochloric acid, whilst with sulphuric acid they give a number which, as in the case of the soluble bases, is 1750 cal. higher than with the two monobasic acids,* so that it may fairly be inferred that they behave towards the various acids in the same manner as the soluble hydroxides do, and would yield the same heat of neutralisation, if only they could be operated on in the dissolved state.

Now the operations which are involved in the neutralisation of an alkali by an acid are numerous. The potash and the acid are each *un*dissolved and decomposed, while the salt and a certain amount of water are formed, these being then dissolved in the excess of water present. Thus,

$$-(\mathrm{KOH,aq}) - (\mathrm{K,OH}) - (\mathrm{HCl,aq}) - (\mathrm{H,Cl}) + (\mathrm{K,Cl}) + (\mathrm{KCl,aq}) + (\mathrm{H,OH}) + (\mathrm{H_2O,aq}) = \mathrm{N} \text{ (heat of neutralisation).}$$

the term $(\mathrm{H_2O,aq})$ being $= 0$.

It is important to bear in mind that, since all the reagents and products are in the liquid condition throughout, the terms (KOH,aq), (KCl,aq), &c., represent the heat evolved by the reaction of a molecule of *liquid* potassium hydroxide, chloride, &c., with excess of water; and it must also be remembered that there is not a single term in the whole equation (except N) of which we have the slightest knowledge, these symbols representing, as properly they should always do, true atoms and simple molecules.

Now N is independent of the nature of the base: sodium hydroxide yields the same results as potassium hydroxide: or, in thermochemical language,

$$-(\mathrm{KOH,aq}) - (\mathrm{K,OH}) - (\mathrm{HCl,aq}) - (\mathrm{H,Cl}) + (\mathrm{K,Cl}) + (\mathrm{KCl,aq}) + (\mathrm{H,OH}) + (\mathrm{H_2O,aq}) = -(\mathrm{NaOH,aq}) - (\mathrm{Na,OH}) - (\mathrm{HCl,aq}) - (\mathrm{H,Cl}) + (\mathrm{Na,Cl}) + (\mathrm{NaCl,aq}) + (\mathrm{H,OH}) + (\mathrm{H_2O,aq}),$$

which may be simplified into

$$(\mathrm{K,Cl}) + (\mathrm{KCl,aq}) - [(\mathrm{Na,Cl}) + (\mathrm{NaCl,aq})] = (\mathrm{K,OH}) + (\mathrm{KOH,aq}) - [(\mathrm{Na,OH}) + (\mathrm{NaOH,aq})].$$

In the same way, the results of neutralising the same alkali with two different acids, such as HCl and HBr, give us

$$(\mathrm{Na,Cl}) + (\mathrm{NaCl,aq}) - [(\mathrm{H,Cl}) + (\mathrm{HCl,aq})] = (\mathrm{Na,Br}) + (\mathrm{NaBr,aq}) - [(\mathrm{H,Br}) + (\mathrm{HBr,aq})],$$

---

* See footnote, p. 598.

both results being expressed by the general equation

$$[(M,R) + (MR,aq)] - [(M',R) + (M'R,aq)] = [(M,R') + (MR',aq)] - [(M',R) + (M'R',aq)],$$

or, more simply,

$$M,R,aq - M',R,aq = M,R',aq - M',R',aq,$$

in which R and R′ represent two negative radicles (hydroxyl included), and M and M′ represent an equivalent of any metal or hydrogen.

Thus there is a constant numerical difference between two metals, independent of the negative radicle with which they are combined, and there is a constant numerical difference between any two negative radicles, independent of the metal with which they are combined, *provided*, always, the compounds are in presence of excess of water.

By combining various pairs of metals and radicles, we could get some hundreds of equations agreeing with this general equation, and, as Nicol says, it is absurd to suppose that this agreement is accidental. Yet the conclusion which he draws from this agreement—that dissolution is not an act of chemical combination—is based in reality on the assumption that it *is* accidental. The equation holds good only if excess of water is present; it is not in the combination of the simple atoms K and Na with Cl, as compared with K and Na with OH, that any simple numerical relation can be found; it is only when we regard as *one* quantity the heat evolved in these combinations and that evolved in the dissolution of the compound in water that a relationship becomes apparent. Each term in the last equation is made up of two quantities, (M,R) and (M,R,aq), one, (M,R), is certainly a chemical reaction, and if the other, (M,R,aq), be, as Nicol maintains, a purely physical reaction, independent of the chemical properties of the compound, it must be a mere matter of chance that the sum of these two independent quantities should in so many cases produce identical results. Such a chance cannot be admitted. The two reactions, (M,R) and (M,R,aq), must be integral parts of one and the same reaction, and if the part (M,R) is a chemical reaction, as it undoubtedly is, so also must be the other part.* The one atom (say

---

* The only way, other than by mere chance, in which these equations might be produced, if the formation and dissolution of the salt were independent actions, would be if

$$M,R - M',R' = M,R' - M',R' \text{ and}$$
$$MR,aq - M'R,aq = MR',aq - M'R'aq;$$

but we have not the slightest grounds for making such a supposition, the simple fact that our neutralisation equation becomes less and less true as the proportion of water present is diminished, would alone warrant the conclusion that it would

M or M′) does not entirely saturate the other atom (R or R′), but leaves it with some energy, or as we call it affinity, still unsaturated, which becomes saturated by the water, if this be present in sufficient excess. In other words, the simple molecules MR, &c., possess some *residual affinity*.

In December, 1885, I brought before this Society my views on atomic valency. The valency of an atom cannot, I considered, be represented by a whole number, as we ordinarily represent it, but is slightly larger or smaller than that whole number; consequently, a compound formed from an atom with a valency 1·1, with another with a valency of 0·9, will not be entirely saturated, but will exhibit a certain amount of residual affinity, represented by (1·1 − 0·9) = 0·2 valency, and it is by means of this residual affinity that it combines with other molecules exhibiting also a residual affinity, thereby forming a so-called molecular compound. As pointed out at the time, it would not necessarily follow that this molecular compound would itself be entirely saturated, but might still retain a small amount of residual affinity, which could only be perfectly saturated by the combination of a large number of these compound molecules with a large number of some other molecules; that such complex aggregates of molecules and of compound molecules do exist, I have recently insisted on several occasions, and it is in their existence only that we can, I think, find an explanation of the nature of solution, and many other similar facts (*Chem. News*, **54**, 216; *Chem. Soc. Proc.*, 1887, 41).

The phenomena observed in the heat of neutralisation afford, I imagine, positive proof of the fundamental conception of this theory,* —the unsaturated nature of simple atomic compounds, and the gradual saturation effected by their combination with other molecules, to form more and more complex systems till saturation be perfect,—a conception which also involves the idea of the valency of any atom being a divisible quantity.

The possibilities of the case may be further investigated as follows:—

1. Each valency is a whole number, and, if saturated at all, is perfectly saturated.

---

not hold at all if no water were present, that is, that M,R − M′,R would not be equal to M,R′ − M′R′.

* In the paper here alluded to, I considered the valencies of the atoms not to be whole numbers, and the atoms with the smaller valencies to be entirely saturated by those with the larger valencies; but the conclusions drawn would hold equally good were we to consider the valencies to be whole numbers, but that two atoms in combining do not entirely saturate each other's affinity: this represents Armstrong's view of residual affinity. [N.B. I take "valency" to be the number which represents the value of the energy or affinity of an atom.]

This is tantamount to saying that there is no such thing as residual affinity, and that M,R − M′,R = M,R′ − M′,R′; which we have every reason to believe is not so (see footnote, p. 595). This hypothesis is, therefore, untenable.

2. Each valency is a whole number, but the affinity which it represents is saturated to different extents by different atoms.

   In this case, if the water saturates the residual affinity, of both metallic and non-metallic atoms, the equation M,R,aq − M′,R,aq = M,R′,aq − M′,R′,aq would not obtain, whereas, if it saturates that of either the metallic or non-metallic atoms only, all the four terms of the equation will be equal. We have no satisfactory reasons for regarding this as either probable or impossible, but from certain considerations derived from a study of the heat of formation of the haloid acids, I am inclined to regard it as improbable.

3. Each valency is not a whole number, but the atom with the smaller affinity is entirely saturated by that with the larger affinity.

   The results in such a case will be similar to those in the following case, but this supposition is scarcely tenable, for, according to it, atoms possessing the same affinity would entirely saturate each other: but, this is not so; elementary molecules exhibit residual affinity. (See Pamphlet on "Atomic Valency," 1885, p. 17, footnote.)

4. Each valency is not a whole number, and when two atoms combine they do not necessarily saturate each other to the full extent of their valencies.

   Our equation, however, will not hold good in the event of the water of solution saturating the valencies of both metallic and non-metallic atoms, it must saturate either the former only—in which case M,R,aq = M,R′,aq, and M′,R,aq = M′,R′,aq —or else (as appears to me most probable), the latter only, in which case M,R,aq = M′,R,aq, and M,R′,aq = M′,R′,aq.

These important conclusions may appear to rest on the assumption of the identity of affinity with the heat of combination; in reality however, no assumption is made; the argument holds good, if not for affinity, at any rate for some energy exhibited by atoms, each atom possessing either exactly, or nearly exactly, one, two, three, &c., units of this energy, according as it is monad, dyad, or triad, and it is owing to its possessing such that it is capable of combining with one, two, or three monad atoms; the terms affinity and valency imply no more than this, and if we use the terms energy and unit of energy, we may discard the others as superfluous. Anyone who has studied thermochemistry must have been impressed by the intimate connection between valency (as ordinarily understood) and heat evolved. On comparing many series of similar reactions, such as the action of water on metals, or the influence of temperature on the heat of dissolution of salts, we find that the heat evolved, or the rate of change, is roughly proportional to the valencies of the atoms concerned,* and our present study of the results of neutralisation simply proves that this proportionality is not merely approximate, but exact.

The fact that a large number of acids give the same heat of neutralisation with bases being due to the residual affinity of the (let us say for the sake of simplicity) negative radicles being entirely saturated by the water present, what explanation can be given of the fact that some acids yield a higher, and others a lower, heat of neutralisation?† It must be remarked that the deviation from the average in these exceptional cases is very small, especially when we consider that the heat of neutralisation is merely the difference between quantities of very great, though unknown, magnitude, and that the water used in the determination was not infinite in quantity as it should have been theoretically.‡

In cases where the heat of neutralisation is greater than the normal, such as—

$$\mathrm{Na,Cl,aq} - \mathrm{H,Cl,aq} = \tfrac{1}{2}(\mathrm{Na_2,SO_4,aq}) - \tfrac{1}{2}(\mathrm{H_2,SO_4,aq}) - x,$$

we may explain the fact by SO_4 possessing more residual affinity when combined with H_2 than the water is capable of saturating, whereas, when combined with metals, the residual affinity does not exceed the quantity which water can saturate; x would therefore be independent of the nature of the metal, which, with certain reservations, is true.§ Other explanations based on the supposition of

---

* I have shown elsewhere (*Phil. Mag.* [5], 23, 109), in a rider to Dr. Armstrong's criticism of Thomsen's thermochemical results with organic substances, that those results tend to give this dynamical conception to affinity in spite of Thomsen's conclusions to the contrary.

† The exceptional cases, those showing a deviation of over 1000 cal., are HF, 16270: HPH_2O_2, 15160; H_2SO_4, 15690; $H_2S_2O_4$, 15145: H_2S, 7740; HClO, 9980; HCN, 2770; H_2AsO_4, 6890; H_2SiO_3, 5230; H_2SnO_3, 9570; H_2CO_3, 10090; $H_2B_2O_4$, 10005; $H_2C_4H_4O_4$, 12080; $H_2C_4H_4O_6$, 12655; H_3PO_4, 11343; H_2AsO_4, 11973; 16 acids out of the 45 which were investigated.

‡ With more dilute solutions, the excess of the heat of neutralisation with sulphuric acid over that with hydrochloric acid would be reduced by at least 400 cal., taking Thomsen's results on the dilution of the various acids and solutions of salts.

§ The values are as follows:—

K......................	1895 cal.
Na	1945 „
Li	1795 „

changes in the mutual relationship between the S and the O_4, according as the radicle is combined with H_2 or M_2, would equally account for the observed facts.

A similar explanation, however, would not apply in cases where the heat of neutralisation is less than the normal (that the residual affinity of MR is not entirely saturated by the water), unless x were different with different metallic radicles, and this is probably not so. I am inclined to regard these exceptionally low results as being apparent rather than real. Seven out of the twelve acids are eminently unstable, and form salts which are more or less dissociated in solution, and, although Thomsen determined the heat of neutralisation when the proportion of base was in excess of that required by the chemical equation,[*] it would not follow that such an excess would increase the proportion of undecomposed salt in the liquid, for he increased the quantity of water present *pari passu* with that of the base. If a portion only of the acid and base are combined, we shall be comparing

$$(M,Cl,aq - H,Cl,aq) \text{ with } \frac{1}{n}\text{th of } (M,R,aq - H,R,aq),$$

and hence the deficit x; moreover, the value of n, and consequently of x, will be independent of the nature of M, since this depends on the relative "affinity" or "avidity" of R and OH, which, according to Ostwald, and (as far as the cases under discussion are concerned) according to Thomsen also, is the same whatever the base may be.

From the general fact that the heat of neutralisation is independent of the nature of the base, it follows that the heat of formation in solution of the same salts of two different metals differs by a constant quantity independent of the nature of the salt. Thus the heat of formation of potassium chloride from metallic potassium and gaseous chlorine is given by the equation—

$$(Na_x + aq) + \tfrac{1}{2}(H_2 + Cl_2) + (NaOHaq + HClaq),$$

Tl	1805 cal.
NH_4	1805 „
½Sr	1540 „
½Ca	1620 „
½Mg	1765 „
½(Mn, Ni, Co, Fe, Cd, Zn or Cu)	1730 „

the higher values obtained in the case of the monad metals can scarcely be accidental, and, I think, they are probably due to there being some small mutual attraction between the two metallic atoms in M'_2SO_4; this is supported by the fact that when we come to pseudo-triad metals, where an attraction of this nature is undeniable and of considerable magnitude, the value of x is entirely different from the above values, and is also different in each individual case.

[*] The values given with excess of base are in some cases considerably higher than those quoted above.

while that of the potassium salts is given by the same equation, in which (K_x + aq) is substituted for (Na_x + aq); thus the difference between the heats of formation of all similar potassium and sodium salts in solution, is simply that existing between the reactions of potassium and sodium with excess of water.* The latter are therefore quantities of fundamental importance. They are :—

Lithium		49084	cal.
Potassium............		48100	„
Sodium		43450	„
Magnesium..........	2 ×	40345	„
Calcium	2 ×	40500	„
Strontium	2 ×	44725	„
(Barium..............	2 ×	40500	„)
Cadmium	2 ×	− 4995	„
Zinc	2 ×	3305	„
Manganese	2 ×	11090	„
Iron	2 ×	− 2645	„
Nickel	2 ×	− 6271	„
Cobalt	2 ×	− 5708	„
Copper	2 ×	− 6470	„

For magnesium and for cadmium and the metals following it, the value is not obtained directly, but indirectly from the heat of dissolution of the metal in hydrochloric acid, this value being subtracted from 2N (27600 cal.). The smallness of the differences between the values given by the first seven metals is very noticeable.

The heats of formation of two similar salts of different metals in the solid condition show no constant difference of this nature; they are calculated by subtracting the heat of dissolution of the salt from its heat of formation in solution, and no strict connection has yet been discovered between the heat of dissolution and the nature of the metal present.

The conclusions derived then from a study of the heat of neutralisation are briefly :—

1. That the heat evolved in chemical combination is strictly proportional to the affinity saturated, and that the heat which we measure represents the algebraic difference between the affinities saturated in the compound and those saturated in the reagents.

2. That atoms in combining do not (in most cases) entirely saturate each other, but that the molecules formed exhibit a certain

---

* From certain discrepancies which exist in Thomsen's numbers, in vol. iii, he does not appear to have been fully aware of this.

amount of residual affinity capable of being saturated by further combination with other molecules.

3. That the atom possessing the smaller valency is not (necessarily) entirely saturated by that possessing the higher valency.

4. That it is due to the residual affinity of either the non-metallic or metallic radicle in a salt molecule, and not to that of both radicles, that water becomes attached to the salt. If the atomic valencies are whole numbers, the four terms, M,R,aq; M′,R,aq; M,R′,aq; and M′,R′,aq, will all be equal, whereas, if they are not whole numbers, each of these terms will be equal to one only of the others.

Lastly, that the dissolution of a salt in water is a chemical and not a physical action.

LVII.—*Crystals in Basic Converter Slag.*

By J. E. Stead and C. H. Ridsdale.

In the course of some investigations made at the works of the North Eastern Steel Co., Middlesboro', as to the nature and constitution of slag obtained by the "Basic" or "Thomas-Gilchrist" process, we found several distinct varieties of crystals, some of which are of a composition hitherto quite unknown, and all are comparatively new.

We believed, therefore, that a brief description of them would not be without interest to the members of this Society.

The slag itself is the product of the oxidation by the Bessemer process of the impurities of phosphoric pig (Si, P, Mn, V, Cr, &c.), and also of part of the iron, admixed with the flux (lime) added to the fluid iron treated, and with part of the dolomite-lime lining of the converters which is worn away in the treatment of each charge. It consists, as will be shown, principally of phosphate and silicate of lime and magnesia, together with excess of lime and magnesia in the free state, and oxides of iron and manganese.

The North Eastern Steel Co. slag, from which the crystals were obtained, contains usually—

CaO.	MgO.	Al_2O_3.	FeO.	Fe_2O_3.	MnO.	VO.	SiO_2.
45·04	6·42	1·50	2·10	15·42	3·50	1·35	5·80

S.	Ca.	SO_3.	P_2O_5.	Total.
0·32	0·40	trace	18·10	99·95

Metallic iron	13·46
" manganese	2·71

Its composition varies, however, according to the pig iron used, and with the extent to which the iron is oxidised during the process; the nature and amount of the basic addition made to the charge, and the proportion of the lining worn away, also affects it, but as a rule the Company's slag varies but little in composition, the phosphoric acid never being below 17 nor above 20 per cent.

The crystals were invariably found near the centre of blocks of slag, each of which weighed between 40 and 50 cwt. As the masses of slag solidify on the surface as they cool, contraction could only obtain in the interior, the result being in every case that a cavity was formed in the centre, about which the crystals were formed.

We shall now describe the various crystals separated.

No. 1. These are large, well-formed, flat, square crystals, some of which have V-shaped edges. They are perfectly transparent, and of a faint yellowish colour—when thin nearly colourless.

Their analysis is as follows:—

Lime	60·206
Magnesia	0·828
Alumina Peroxide of iron	0·100
Protoxide of manganese	trace
Vanadium protoxide	0·722
Silica	trace
Sulphur	0·150
Phosphoric acid	38·044
	100·050
Less O replaced by sulphur	0·075
	99·975

Their composition is probably that of tetrabasic phosphate of lime, $4CaO·P_2O_5$	CaO, 60·013 P_2O_5, 38·044	98·057
(0·069 per cent. too little CaO for the above after satisfying S.)		
Calcium sulphide (= 0·262 CaO)	Ca, 0·15 S, 0·187	0·337
Magnesia		0·828
Alumina and peroxide of iron		0·100
Protoxide of vanadium		0·722
		100·044
Less excess of CaO required for P_2O_5		0·069
		99·975

They appear to be tetrabasic phosphate of lime, and were described by Hilgenstock at the *General Vesammlung des Vereins deutscher Eisenhüttenleute*," in June, 1886; an account and a reprint of his paper was circulated at the Autumn Meeting of the Iron and Steel Institute the same year; at this meeting Mr. Stead exhibited them on our behalf, together with several other varieties, and mentioned at the same time that we had been investigating them since March, 1886 We wished, however, to prosecute our investigations more fully before reading a paper on them.

No. 2. Groddeck and Broockmann describe these in *Stahl ünd Eisen*, 1884, No. 3, p. 141, as "rhombic, partly columnar and partly tabular blue crystals," and give their analysis as

CaO.	MnO.	FeO.	P_2O_5.	Total.
56	3	6	35	100

but they state that they "had great difficulty in getting enough for analysis," and that they were "so small that their form could only be seen with a microscope." We have, however, been able to get them from one-twenty-fourth to one-sixteenth inch in diameter, and by breaking the picked crystals down small and repicking with the aid of a magnifying glass, rejecting every piece that had the slightest trace of any other crystalline form attached, we believe that we obtained them almost absolutely pure.

These were amongst the crystals exhibited, and noticed on our behalf by Mr. Stead at the Iron and Steel Institute, 1886. The composition of different crops of pure samples was constantly as follows:—

	Per cent.
Lime	56·578
Magnesia	0·738
Alumina	trace
Peroxide of iron	1·000
Protoxide of manganese	0·210
Oxide of nickel	0·040
Sesquioxide of chromium	trace
Protoxide of vanadium	1·640
Silica	10·791
Sulphur	0·055
Phosphoric acid	29·146
	100·198
Less O replaced by S	0·027
	100·171

		Per cent.
Tetrabasic phosphate of lime	CaO, 45·976 P_2O_5 29·146	75·122
Calcium silicate............	CaO, 10·071 SiO_2, 10·791	20·862
Calcium sulphide	Ca, 0·07(0·098CaO) S, 0·055	0·125
Magnesia....................................		0·738
Peroxide of iron		1·000
Manganous oxide..............................		0·210
Nickel oxide		0·040
Protoxide of vanadium		1·640
Lime not accounted for.........................		0·433
		100·170

The greater the care taken in separating the crystals from the matrix, the lower the percentage of iron and manganese oxides found in them, and as the substances they were mostly contaminated with, when found, were magnetic black crystals—of which more anon—we think this will account for Groddeck and Broockmann finding so much ferrous oxide and manganous oxide. The silica they probably missed through working on so small a quantity, but we have invariably found from 10 to 11 per cent., from which it would appear that these forms consist of a double phosphate and silicate of lime, coloured by traces of impurity. They frequently occur in proximity to masses of steel. These blue crystals are readily melted before the oxyhydrogen blowpipe flame, to a cream-coloured enamel-like mass, with no blue coloration, from which we deduce that the colour is due solely to some molecular arrangement peculiar to the crystalline form.

No. 3. These are feathery or fern-like crystals, of which Groddeck and Broockmann in a passing notice say, "it would be extremely difficult to obtain sufficient for chemical and crystallographic examination," and they consequently give no results. We, however, have succeeded in picking out a considerable quantity, and as they are strongly magnetic they were separated from all impurity by first picking quite clean, then subjecting them to magnetic separation. We found them to contain—

		÷ Atomic weight.
Lime	18·732	0·3345
Magnesia	11·456	0·2864
Alumina	1·800	0·0175
Peroxide of iron	16·143	0·1009
Protoxide of iron	38·060	0·5286
„ of manganese	9·580	0·1349
Oxide of nickel	0·150	0·0025
Chromium sesquioxide	1·120	0·5073
Protoxide of vanadium	0·289	0·0021
Silica	0·800	0·0133
Sulphur	0·186	0·0058
Phosphoric acid	1·667	0·0117
	99·983	
Less O replaced by S	0·093	
	99·890	
Total iron	40·90	

Magnetic oxide of iron, Fe_3O_4	Fe_2O_3,	16·164	23·428
	FeO	7·264	
Tetrabasic phosphate of lime, $4CaO{\cdot}P_2O_5$	CaO,	2·625	4·292
	P_2O_5,	1·667	
Calcium sulphide (= 0·32 CaO)	Ca,	0·232	0·418
	S,	0·186	
Free ... CaO (÷ atomic weight.		0·2819)	15·787
Free ... FeO (÷ atomic weight.		0·4277)	30·796

This material is very remarkable as showing so little acid and so much base, there being only 3·693 per cent. acids and 95½ per cent bases.

A magnetic separation only (without previous picking) from a mass of mixed crystals crushed fine, gave an approximate analysis of

CaO.	MgO.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	SiO_2.	P_2O_5.	Total.
30·24	4·40	0·27	24·57	28 30	7·80	0·90	3·73	100 21

which approaches decidedly to the composition of the magnetic fern crystals.

No. 4. These are hexagonal, needle-shaped, lemon-coloured crystals, and do not appear to have been described previously, for although Hilgenstock in his paper to the *Verein deutsche Eisenhüttenleute* mentions "needle-like" crystals, he says they gave the analysis of pure tetrabasic phosphate of lime, from which we infer them to have been similar in colour to the flakes. These, however, are of a greenish-yellow colour, and on being carefully picked, ground, and finally cleaned with the magnet, yield a faint pink or flesh-coloured powder. Different crops of these crystals gave a constant composition as follows:—

	Per cent.
Lime	53·536
Magnesia	0·486
Peroxide of iron	4·857
Protoxide of iron	1·286
„ of manganese	0·790
Chromium sesquioxide	trace
Vanadium protoxide	1·343
Silica	3·900
Sulphur	0·460
Phosphoric acid	33·707
	100·365
Less O replaced by S	0·23
	100·135

				Per cent.
Tetrabasic phosphate of lime, $4CaO \cdot P_2O_5$	CaO,	52·731		86·131
	P_2O_5,	33·400		
Pyrophosphate of magnesia, $2MgO \cdot P_2O_5$	MgO,	0·171		0·478
	P_2O_5,	0·307		
Calcium sulphide (= 0·505 CaO)	Ca,	0·575		1·035
	S,	0·460		
Double silicate of ferrous and ferric oxide, *i.e.*, silicate of magnetic oxide, $Fe_3O_4(SiO_2)_2$	Fe_2O_3,	4·504	5·890	8·550
	FeO,	1·286		
	SiO_2,		2·760	
Silicate of manganese	MnO,	0·79		1·458
	SiO_2,	0·668		
Peroxide of iron not accounted for				0·353
Protoxide of vanadium				1·343
				100·135

Hence they appear to consist of about 86 per cent. tetrabasic phosphate of lime, coloured with 10 or 11 per cent. of silicates of metallic oxides. We know that ferric silicate colours glass yellow, and ferrous silicate greenish-black, and if the iron salts were not combined with the silica, the magnetic oxide being free would have been separated in the successive magnetic cleanings, besides which there would have been 1·999 per cent. peroxide of iron (as it is there are about five parts silicate of peroxide to three parts silicate of protoxide).

Nos. 5 and 6 are two varieties of flat, black, pointed, spear-shaped crystals, both looking almost like graphite flakes, but one is not at al attracted by the magnet, the other is distinctly. The following is their composition:—

	No. 5. Magnetic.	No. 6. Non-magnetic.
Lime	39·088 p. c.	44·730 p. c.
Magnesia	1·297 „	0·936 „
Alumina	6·400 „	9·700 „
Peroxide of iron	33·857 „	35·657 „
Protoxide of iron	8·100 „	none
„ of manganese	1·348 „	1·023 „
Oxide of cobalt	trace	trace
„ of nickel	trace	trace
Chromium sesquioxide	5·980 „	4·200 „
Copper oxide	none	trace
Protoxide of vanadium	2·656 „	2·223 „
Silica	1·100 „	0·900 „
Sulphur and sulphur trioxide	not estimated.	not estimated.
Phosphoric acid	trace	0·740 „
	99·826	100·109
Total iron	30·000	25·10

			Per cent.			Per cent.
Aluminate of lime, $CaO{\cdot}Al_2O_3$	CaO,	3·486	9·886		5·284	14·984
	Al_2O_3,	6·400			9·700	
Magnetic oxide of iron and lime, $3CaO{\cdot}Fe_3O_4$	Fe_2O_3,	18·00	26·10	45·000		
	FeO,	8·10				
	CaO		18·90			
Peroxide of iron and lime, $3CaO{\cdot}Fe_2O_3$	Fe_2O_3,	15·857	32·507		35·657	73·096
	CaO,	16·650			37·439	
Tetrabasic phosphate of lime, $4CaO{\cdot}P_2O_5$	CaO				1·167	1·907
	P_2O_5				0·740	
Silicate of lime, $CaO{\cdot}SiO_2$	CaO				0·84	1·740
	SiO_2				0·90	
Silicate of manganese, $MnO{\cdot}SiO_2$	MnO,	1·32	2·420			
	SiO_2,	1·10				
Magnesia			1·297			0·936
Manganous oxide			0·028			1·023
Chromium sesquioxide			5·980			4·200
Protoxide of vanadium			2·656			2·223
Lime (not accounted for)			0·052			—
			99·826			100·109

They, like No. 3, are remarkable for their small content of "acid," or non-metallic oxides, there being in

Magnetic............ 1·1 per cent., excluding alumina.
Non-magnetic........ 1·64 „

But just as alumina can sometimes act as an acid, and sometimes as a base, according to the basicity of the element with which it is combined, so it seems possible for ferrous, ferric, and magnetic oxides to combine with lime under certain conditions, and to behave *relatively to lime* as an acid. We are not aware that such a combination has ever been met with before, but, on the other hand, there probably never were such favourable conditions on a large scale as the basic process affords for their formation, both as to intense temperature and large excess of basic materials.

Crystals from the Basic Slag.

By H. A. Miers, M.A., F.G.S., Natural History Museum.

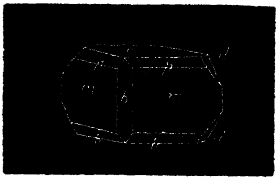
No. 2. *Blue Crystals.*—These appear in the form of thick tables or stout prisms, sometimes with bright smooth faces, but more frequently skeletal and formed by the superposition of laminæ.

The result of gonimetrical measurement is as follows:—

System orthorhombic.

$$a : b : c = 1·5023 : 1 : 2·2943,$$

corresponding to the angles 100 : 110 = 56° 21′; 010 : 011 = 23° 23′; 001 : 101 = 56° 47′.



Forms observed:
$m\{110\}\infty P.$
$c\{001\}0P.$
$d\{101\}\breve{P}\infty.$
$p\{111\}P.$
$b\{010\}\infty\bar{P}\infty.$
$r\{103\}\frac{1}{3}\breve{P}\infty.$

A face of the form r was only once observed.

A large number of crystals were measured, but the angles given below are the means of those formed by such faces alone as gave single bright images, so that the individual measurements could be relied upon to two or three minutes.

The angles *cd* and *dm* were used as the basis of calculation.

	Observed.	Calculated.	No. of edges.	Limits.
cd..	56° 47′	—	7	56° 38′—56° 51′
dm	62 23	—	6	62 19—62 31
mm.........	67 11	67° 18′	5	67 6—67 18⅓
dp	51 31½	51 29½	1	—
cp..........	70 4½	70 3¼	1	—
cr..........	26 40	26 59	1	—

The crystals exhibit a very marked and most beautiful pleochroism; viewed through the faces *c* by plane polarised light transmitted in the direction of the vertical axis they appear deep sapphire-blue when the light is polarised in a plane parallel to the macropinacoid, and a very faint lilac when the light is polarised in a plane parallel to the brachypinacoid; viewed through a plate cut parallel to the macropinacoid *b*, they appear faint blue when the plane of polarisation is parallel to the vertical axis, and a somewhat deeper blue when it is parallel to the basal plane *c*.

Plane of the optic axes parallel to 100; acute bisectrix perpendicular to *c*; axial angle measured in oil 114° 30′ (about).

No. 4. *Yellow Needles.*—These are six-sided prisms, with a prism angle of 60°, and are uniaxial, sections cut perpendicular to the prism remaining dark between crossed Nicols. They are therefore to be referred to the hexagonal system. They contain fine linear enclosures, which, together with the cleavage cracks, appear to be parallel to the faces of a pyramid $P\{100, 22\bar{1}\}$, if the prism be denoted by the symbol $\infty P2\{10\bar{1}\}$. Calculations from the angles which these lines make with the prism edges upon the different prism faces measured with a rotating stage under the microscope show that this pyramid is inclined to the vertical axis at an angle of about 54° 30′ (limits 53° 50′—56° 0′).

The only faces, however, which are developed upon the crystals are the prism and the basal planes 0P.

These needles show marked dichroism, appearing light yellowish-brown when parallel to the plane of polarisation, and a darker clove-brown when perpendicular to the same.

No. 1. *Brown Tables.*—These appear to be orthorhombic; they form rectangular tables, bearing on their edges linear faces inclined at angles 51° 25′ (limits 50° 19′—51° 54′) and 59° 10′ (limits 59°—59° 20′), respectively to the faces of the table; there are two imperfect cleavages perpendicular to the table and parallel to its edges of intersection with the linear faces. The crystals are faintly dichroic.

LVIII.—*Ozone from Pure Oxygen: its Production and its Action on Mercury, with a Note on the Silent Discharge of Electricity.*

By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College, and J. TUDOR CUNDALL.

FOR the purposes of some experiments we are making with the hope of obtaining further information concerning the influence of the silent discharge of electricity on oxygen and other gases, we have had occasion to prepare oxygen gas of a high degree of purity and to transfer it to experimental apparatus of various kinds without contamination. We have taken the opportunity which has thus occurred to make the experiments that we now have the honour of describing to the Chemical Society.

In their classical research, "On the Volumetric Relations of Ozone," Andrews and Tait (*Phil. Trans.*, 1860, Part I, p. 113) have already shown that ozone may be produced from oxygen of considerable purity. They express their opinion that not more than one part of nitrogen was present in every thousand parts of the oxygen they employed, and, though they do not describe any analyses in support of that opinion, there can be no doubt that the gas employed was more than sufficiently pure for the object they had before them, viz., to establish the elementary nature of ozone. But, taking into consideration the fact that unprotected india-rubber connections were employed in some parts of their apparatus, and that they dried the gas merely by passing it over fragments of glass moistened with sulphuric acid, it seems improbable that they operated upon oxygen free, in the highest attainable degree, from nitrogen and moisture. The experiments described by Brodie (*ibid.*, 1872), although also made with great care and delicacy, probably were not made with oxygen of the highest attainable purity. In consequence of the interest which now attaches to the chemical behaviour of substances in an extremely pure state, it seemed desirable to repeat experiments like those of Andrews and Tait with all the additional precautions that have become possible.

Whilst we were still engaged in constructing the apparatus presently to be described, a paper on the production of ozone, by Professors J. J. Thomson and R. Threlfall was read before the Royal Society (*Proc. Roy. Soc.*, 1886, **40**, 340). In this paper, it is stated that ozone is formed in large quantities when an electric spark passes through dry oxygen. In the experiment described, however, air was employed, not oxygen, and no details are given in the paper of the mode of recognising the ozone, of the quantity produced, or of the behaviour of dry ozone to any other substance in a dry state; therefore we considered that the subject still deserved careful examination.

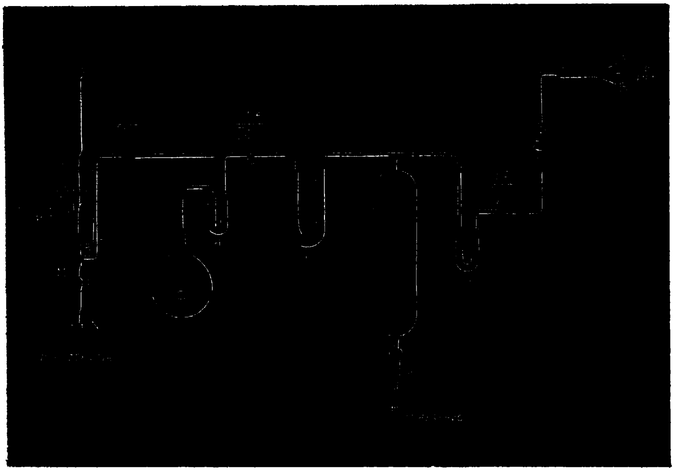
I. *The Preparation and Storage of Oxygen.*

After constructing and trying various apparatus for this purpose, we adopted that which was described at the Birmingham Meeting of the British Association (*Brit. Ass. Report*, 1886), by the aid of which two of the specimens of oxygen used for our experiments were prepared. But further experience in constructing glass apparatus on a large scale has enabled us now to adopt a modification of that apparatus, which affords a far more complete guarantee of the purity of a gas prepared within it after it has been stored for considerable periods of time than was the case with the original simpler arrangement.

In dealing with gases containing less than one part of impurity per thousand, the mode of preparing and storing the gas affords an indication of its quality which is at least as important as any evidence that can be derived from analysis. This consideration will excuse us if we seem to devote a disproportionate part of our paper to a description of the apparatus we now employ.

The general form of the apparatus is shown in Fig. 1. All its parts have been united by welding in the blowpipe flame, except that the sampling tube K is attached by a ground joint at L, which is protected by a cup of mercury with a layer of almond oil above it. The Sprengel pumps attached to C and D also are not only welded to the main apparatus, but were themselves entirely put together by blown joints. The taps employed are those known in this country as Cetti's patent, air is prevented from entering the apparatus by cups of mercury and oil as shown in the diagram. Further, the mercury which is introduced into various parts of the apparatus from time to time passes in all cases through efficient air-traps. It appears, therefore, to be impossible for air to gain admittance to any gas that may be stored within the apparatus so long as no part of the glass work is broken. As a rule, we find that air-traps such as G (Fig. 1) answer very well, but occasionally air collects in a trap with inconvenient rapidity, and we think the trap shown at L is more satisfactory. In this form of trap, which we do not remember to have previously seen described, there is attached at the shoulder a narrow tube M, drawn out at its upper end. When air has collected at L, it can be expelled, without admitting air to the store of gas within the apparatus, by opening the tip of M and raising the reservoir of mercury attached to the india-rubber tube N.

FIG 1.



For generating oxygen, E is charged with a mixture of the chlorates of sodium and potassium in molecular proportions. This is prepared by fusing the two salts together, and powdering the mixture after it has solidified on cooling. We find this mixture a very convenient source of oxygen on account of its low melting point, provided care be taken to employ sodium chlorate that is perfectly free from the tartrate.

To fill the apparatus in the first instance, F is filled with mercury from a reservoir not shown in the diagram, the taps t^1, t^2, t^3 are opened, and the apparatus is well exhausted by the Sprengel pumps attached to C and D. Oxygen is then generated in E until the whole apparatus, including F, is filled. It is then re-exhausted, refilled, and left with its charge of oxygen for several days in order that any nitrogen adherent to the glass may, as far as possible, be removed by the molecular impacts of the oxygen; lastly this charge of gas is also removed, and the final charge is generated from the chlorates in E. A simple calculation shows that if the pumping apparatus only removes $\frac{759}{760}$ of the contained gas at each operation the amount of nitrogen present in the oxygen thus prepared will be about $\frac{1}{1000000000}$ of the whole. After the apparatus has been once charged, when the supply of oxygen remaining in F becomes small, t^2 is closed, t^1 is opened, and E is heated as before. The first portions of oxygen evolved are permitted to escape by D through the fall tube of the Sprengel pump, and so soon as all fear of accidental admission of air in consequence of the breaking of E is past, t^1 is closed, t^2 opened, and F filled as before. The taps have been very carefully reground, and we find that they resist the passage of air excellently, so that in case of E breaking we believe it might be replaced and its contained air removed without any sensible contamination of the gas ready for use in F. As we have been fortunate in our selection of flasks, however, we have not had occasion to put this opinion to the test of an experiment. The tube H contains glass wool which filters out suspended particles of salt from the gas. I is a large U-tube containing solid potash to absorb any minute trace of carbon dioxide that might accidentally be evolved in consequence of the presence of carbonaceous particles in E. As we adopt every possible means of avoiding this in preparing the chlorates, and as the chlorates in E are kept in a fused condition for a considerable period before E is fixed in its place, the necessity of I is doubtful.

We have repeatedly examined considerable quantities of our gas for such impurities as carbon dioxide and chlorine, but have never obtained any indication of their presence.

O contains phosphorus pentoxide, but the employment of this substance is not related to the experiments we are about to describe. Various pieces of apparatus have been attached to A and B temporarily or permanently as was required.

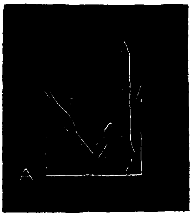
2. *Testing the Purity of the Gas.*

As we have remarked above, there is a strong presumption that the proportion of nitrogen present in oxygen prepared as we have described it is so small as to be far beyond measurement. We have thought it right, however, so far as possible, to test the truth of this assumption.

Specimens of gas for examination may be obtained from time to time in sampling tubes, such as K, capable of holding about 30 c.c. of the gas. Our method of filling them has been to let the gas be free to diffuse throughout all parts of the apparatus for many hours, then to close t^1, and after slightly reducing the pressure in K by the pump attached to D, to carefully seal off K at *q*, where the glass is well thickened beforehand, in order that it may not collapse irregularly when softened. A fresh tube is afterwards put in the place of K, by filling the trap R to the level TT with mercury, removing the stopper from L, welding to it another tube, replacing the stopper in L, and exhausting and filling this tube with oxygen as previously described, the mercury in the trap serving to protect the stock of gas from contamination meanwhile. We also attach various pieces of apparatus that we require to fill with oxygen by means of L.

The tube *k* containing the sample of oxygen is placed with its thin expanded end downwards in a *glass* vessel of mercury, A, which has been previously thoroughly freed from air bubbles, heated on a sand-bath, and then allowed to cool (Fig. 2). The thin glass is easily broken by pressing it on the bottom of A, and a little mercury enters the tube. Reagents are then introduced. For some time, we had great difficulty in securing a suitable reagent for our purpose; the best of those ordinarily employed, even when prepared with the greatest care, left a residue which seemed to indicate the presence of about one part of nitrogen in one thousand parts of the gas. After several failures, it occurred to us that phosphorus, though in most cases an unsatisfactory absorbent of oxygen, would not be unsuitable in the case of pure or nearly pure oxygen. In using phosphorus, however, we find that the greatest care must be taken not to permit moisture to accompany it, because the presence of a very small quantity of water results in the production of a sensible volume of a fixed gas, which we are inclined to suppose to be phosphine. The method which has given us the best results is as follows:—Melted phosphorus is drawn into a pipette P, which has a very long and rather wide end at *b*. It is then boiled for some time to expel moisture, and the end *b* is sealed at C. The basin of mercury in which *k* has been opened is then placed upon a tripod support, the pipette P brought into the position shown in Fig. 2, and its end broken off at *d* without exposing the phosphorus to the air; the tip of the pipette is then brought

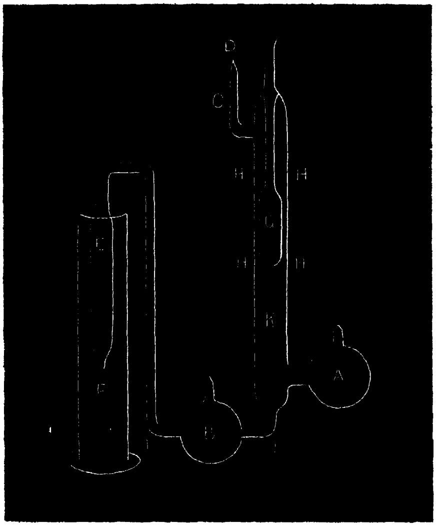
FIG. 2.



under the mouth of *k*, and the mercury is warmed till the phosphorus melts; a little of it is then forced out of the pipette. Heat is cautiously applied to *k* till the phosphorus is ignited, if that does not at once occur. Finally *k* is heated so that vapour of phosphorus fills the space previously occupied by oxygen. The whole is then allowed to cool, the extremely minute space occupied by the residual gas noted, and its volume determined by filling it with water which is afterwards weighed. As the volumes to be measured are very small, the results can only be regarded as close approximations. If the phosphorus employed has not been thoroughly dried by boiling, not only is the volume of residue somewhat greater, but we find that sometimes it may be increased by the prolonged action of heat.

A portion of the oxygen we employed in the second pair of experiments now described was tested in this manner. It left a residue amounting to no more than one part in five thousand of the gas. Taking into consideration the very great difficulty of obtaining phosphorus *perfectly free* from air, moisture, and phosphorous acid, we are not inclined to consider that this result indicates that only $\frac{4999}{5000}$ of our gas was oxygen, but rather that the purity of our oxygen considerably exceeds this.

Fig 3



Our first pair of experiments were made on oxygen collected in tubes such as that shown in Fig. 3; they were filled from the apparatus described at the Birmingham meeting of the British Association (*loc. cit.*). Analysis showed that the gas when introduced into them contained not less than 99·96 per cent. of oxygen, and probably a considerably greater proportion. Although several india-rubber connections were used in that apparatus, they were all well protected from the outside air by mercury, and exposed to a vacuum for many hours before any gas was collected in the apparatus, whereby ample opportunity was afforded for the escape and removal of any occluded gas.

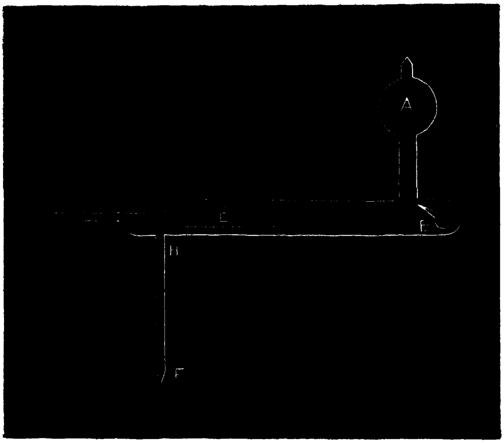
The globes A, B were filled with phosphorus pentoxide, and the two pieces of apparatus were filled with oxygen through C and sealed off at D; in filling them, all the precautions described in connection with the preparation of oxygen were taken. The tubes were then placed in a moderately warm cupboard from June 9th, 1886, to March 31st, 1887. The end of the arm E was then broken under the surface of sulphuric acid in the vessel F, the position of the sulphuric acid in E noted, and the gas electrified by connecting dilute sulphuric acid in G, and a tinfoil envelope at HH with the electrodes of a Rhumkorf coil capable of giving a spark of 4 or 5 inches. As B was closely packed with phosphorus pentoxide in a fine powdery condition, diffusion across it would occur very slowly, and we believe that any minute traces of moisture that might be communicated by the sulphuric acid to the oxygen would scarcely be permitted to pass through B. If we are wrong on this point, however, it will rather give emphasis to our results than detract from their value, inasmuch as we believe the yield of ozone in our experiments with these tubes is decidedly high for the temperature at which the experiments were made. Moreover, the results of a second series of experiments in which our gas was not brought into contact with sulphuric acid or any other possible source of moisture confirm our general result. Under the influence of the electric discharge, a steady diminution of the volume of the gas set in, which continued for a long period of time; doubtless in consequence of the slowness of diffusion across the bulb B. After frequently repeated electrification for short periods during 24 hours, the new position of the sulphuric acid in E was noted, the apparatus cut into three parts at I, I, and the volumes required ascertained in the usual manner. In one experiment, an unfortunate accident to E compelled us to do no more than estimate the contraction that occurred. We were very careful to avoid over-estimation, and came to the conclusion that a contraction corresponding to the conversion into ozone of at least 7·5 per cent. of the oxygen employed had occurred, although the action of the electricity was still incomplete. In a subsequent observation, we learnt, however, that the contraction of oxygen when electrified in contact with sulphuric acid must not be depended on for obtaining an exact measure of the ozone formed, unless certain precautions, which we omitted in this case, are taken. The second tube was treated like the first, except that the gas was electrified at intervals for three days.* The discharge in this tube was, we believe, singularly free from the larger sparks of electricity which reveal their presence by the sound which they produce, and which often accompany the so-called silent discharge. It was, in fact, more nearly a silent discharge than anything we had previously met with. Although the temperature at which we worked was never lower than 10° C., the contraction that occurred was so great as to indicate the conversion of about 15 per cent. of the oxygen into ozone. This led us to doubt the entire trustworthiness of this method of measuring the formation of ozone, which we had copied from Andrews and Tait. And we therefore attached a burette containing turpentine to C by means of an india-rubber tube filled with turpentine and closed by a clamp. Then the end having been broken we allowed a small known quantity of turpentine to flow over the inside of K. The absorption was complete in about an hour, and amounted to 10·25 c.c. The volume of the residual oxygen under the same conditions of temperature and pressure was 116·2 c.c. (the P_2O_5 being neglected), from which we find that the amount of oxygen converted into ozone was 11·7 per cent. of the quantity of oxygen employed in the experiment (a little higher indeed as the volume occupied by the P_2O_5 has been added to the true volume of residual oxygen present). This yield of ozone is high, as no precautions could be taken to electrify the oxygen at a low temperature. This considerably exceeds what is ordinarily produced by the passage of a current of oxygen through a similar apparatus of the Siemens type, our experience being that under similar conditions as to temperature a yield which exceeds 6 per cent. is satisfactory. It is, however, very difficult to obtain concordant results in the production of ozone at different or indeed at similar temperatures. It does not, however, reach the proportion—25 per cent.—which would correspond to the contraction observed by Andrews and Tait in one of their experiments, in which a different mode of electrification was employed. In their experiments, however, oxygen was ozonised in contact with sulphuric acid, and the results, therefore, are almost certainly somewhat high. We have now prepared some tubes of oxygen provided with means of electrification similar to those employed by these observers, and therefore in the course of six months hope to be able to report whether an increased yield of ozone results in this case from the employment of pure and dry oxygen.

---

* The actual period during which the discharge took place considerably exceeded an hour. The temperature of the air at the time of the experiment varied from 10° to 11°. That of the tube at H–H was rather higher.

3. When the apparatus for storing oxygen, described in the earlier part of this paper, was complete, we filled two tubes like that shown in Fig. 4 with oxygen, a sample of which taken at the same time and examined with phosphorus was found to yield only $\frac{1}{5000}$ of residue, and which for the reasons already given we regard as in all probability containing a very considerably smaller proportion of nitrogen than this. A is a chamber containing phosphorus pentoxide, B a small bulb of pure mercury containing neither air nor moisture. One of these tubes filled with the purest oxygen we have yet obtained was kept for seven weeks; the gas within it was then electrified by connecting the poles of the coil with dilute sulphuric acid in E, and tinfoil fixed around the tube from H to H. Afterwards, the bulb B containing the mercury was broken. So soon as this was done, the surface of the mercury lost its convexity, and the mercury adhered to glass in the well-known manner to such an extent that it was easy to attach the remains of the glass bulb to any part of the tube to which mercury adhered. After 24 hours, however, none of the usual signs of oxidation were apparent on the mercury, and after a few days it showed signs of recovering its ordinary condition. The end F of the tube was then attached (by india-rubber) to a wider tube containing paper moistened with potassium iodide and starch solution, its tip broken off, and some of the gas pumped quickly over the test-paper, but no evidence of the presence of ozone was obtained in this way, nor had the gas that remained in the tube any odour of

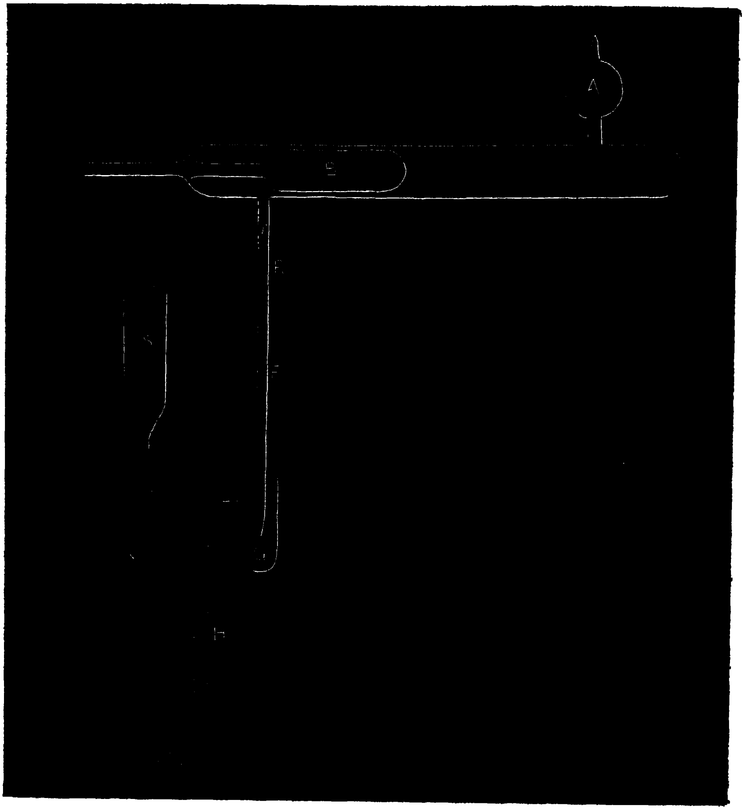
FIG. 4



ozone when we afterwards examined it It is true that the india-rubber connection employed in this case is not entirely satisfactory, but no other suggested itself, and we took care that the gas should rush quickly through it into a partly exhausted space, where it had time to act upon the test employed. We cut up the tube and examined the residual mercury, and found that it could readily be run into *perfectly clean* globules by rubbing together the detached portions with a fragment of wood. This leads us to conclude that perfectly dry ozone is completely decomposed by mercury without the mercury undergoing permanent oxidation. This conclusion is confirmed by subsequent experiments.

It is well known that the distinctive action of ozone on mercury is accompanied by very evident oxidation, and we find that mercury is only capable of thus destroying ozone without itself undergoing some degree of oxidation when the ozone is in a very dry condition. We have passed oxygen generated from chlorate of potassium, and purified by moist and dry caustic potash in a slow stream through an ozone generator, then over a column of phosphorus pentoxide 11 inches long, and then through pure mercury placed in a small washing tube, all air having been previously driven from the apparatus by the passage of a very long-continued stream of oxygen, and have found that on sealing the tube with its contained ozonised oxygen, although scarcely any signs of oxidation appeared after an hour, very decided indications of oxidation developed after 12 hours. Andrews and Tait found that when bulbs of mercury are broken in vessels containing ozonised oxygen, the mercury is oxidised, and an expansion consequent upon the destruction of ozone by the mercury also occurs which, however, never restores the gas to quite its original volume. In the most favourable cases, a permanent contraction, amounting to one-sixth of the contraction on ozonisation, remained. This may have been due to oxidation of the mercury alone or partly also to absorption of ozone by the sulphuric acid employed in the pressure-gauge. In order to confirm or disprove our conclusion, that in our experiment the ozone was entirely destroyed without oxidation of the mercury, we used our second tube of purest oxygen for the modification of the experiment which follows. After the oxygen had been submitted to the drying action of the phosphorus pentoxide in A for eight weeks, the end of the side tube F (Fig. 5) was immersed in mercury that had just before been strongly heated and placed while still warm in the tube G. The tip of F was broken off by pressing it against the sides of G, and F was fixed with a cork in such a position that G formed an air-trap to prevent the entrance of air from H into the pure oxygen. To G an adjustible reservoir S containing mercury was attached. By means of the reservoir this gas in B was

FIG. 5.



brought to a reference mark R, and its pressure, viz., 769·8 mm., and the temperature of the air (12·3°) were observed. The gas was then electrified as before (the level of the mercury in F being slightly reduced). The production of ozone in this case quickly approached the maximum owing, perhaps, partly to its destruction by the mercury in F, but chiefly to a decreased rate of production in consequence of the rise of temperature that occurred about B; for it was not possible to adopt the mode of repeated brief periods of electrification with considerable periods of subsequent cooling, that we employed in the previous experiments, in consequence of the destruction of ozone by the mercury that would have occurred during the periods of delay. After electrification, the pressure required to bring the gas to the mark R was again observed, and was found to be 754·1 mm, a diminution that corresponds to the presence of 6·1 per cent. of ozone in the gas.

As the ozonisation was towards the end conducted at a rather high temperature, and as destruction of the ozone by the mercury must have occurred during the progress of the experiment, and during the cooling down of the tube after the electrification was stopped, this may be regarded as a very good yield of ozone.

The ozonised oxygen was left for twenty-four hours in contact with the mercury in F, which was then repeatedly brought into view by adjusting the position of the reservoir S. We were unable to perceive any signs of oxidation of the mercury even after several days had elapsed.

Although by this time it was no longer possible to observe the mercury in F at the line R (in consequence of the adhesion of the mercury to the glass), and so to ascertain at what pressure the oxygen in the apparatus would now occupy its original volume at 12·3° C., we succeeded in getting a close approximation to this in the following manner:—

Having succeeded in getting the mercury visible at a point near or a little above *r*, the pressure at which the gas occupied this new volume was observed. It was found to be 774·2 mm. when corrected for difference of temperature. A subsequent experiment made, after cleaning the tube, showed that to compress air from R to *r*, a pressure of 5·4 mm. was required: hence 774·2—5·4 = 768·8 was the pressure at which the gas would now fill our tube to the reference mark R As the pressure at which it originally occupied the same volume was 769·8 mm., it appears that of the contraction observed on ozonification (which corresponded to a diminution of pressure of 15·7 mm.), all but so much as corresponds to a pressure of 1 mm. had been restored by the action of the mercury; that is to say, $\frac{1}{16}$ only of the contraction was permanent. When the difficulties under which those measurements were taken are considered, this seems to us to strongly confirm the conclusion we had come to from our examination of the appearance of the mercury in two separate experiments, viz., that when dry ozone is decomposed under the influence of dry mercury, no oxidation of the metal takes place. Andrews observed that the permanent contraction of oxygen which had been ozonised and subsequently treated with mercury was greater in proportion to the suddenness with which the mercury acted. In our first experiment, by disturbing the metal with the fragments of glass, we did our best to hasten the change. In our second experiment, however, it was not possible to do otherwise than permit the change to proceed slowly.

From the experiments we have made we draw the following conclusions:—

1. That pure and dry oxygen is partly converted into ozone by the action of the silent electric discharge.

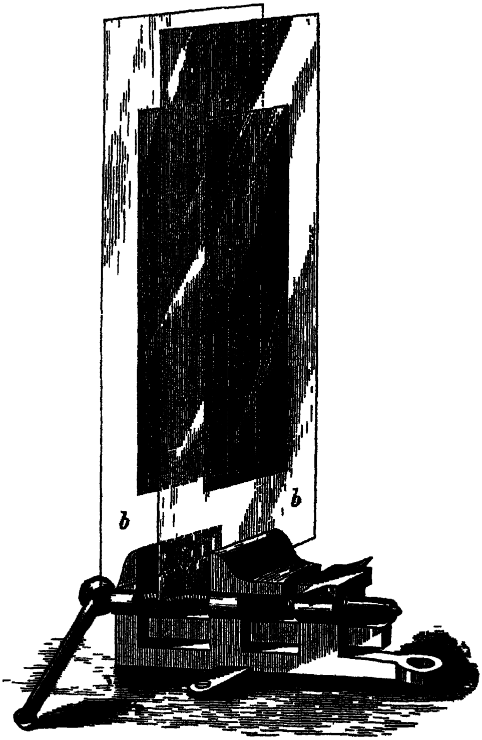
2. That when ozone generators of the Siemens type are employed, the proportion of oxygen converted into ozone in the case of pure and dry oxygen appears to be somewhat greater than in the case of less pure oxygen under otherwise similar circumstances *

3. That dry ozone is completely destroyed by contact with mercury, after some hours, without perceptible oxidation of the mercury, such as occurs to a greater or less extent when mercury and imperfectly dry ozone come into contact.

Note on the Silent Discharge of Electricity.

The influence of purity and dryness on the formation of ozone from oxygen by silent discharge may be due to one or both of two independent causes.

FIG 6



---

* This, however, is based chiefly on our own experience, and it is difficult to compare our work with that of others until the influence of temperature and other circumstances on the production of ozone is better understood than at present.

a. Andrews and Tait (*loc. cit.*) have shown that, if the conditions be such as to favour the combination of nitrogen and oxygen, the presence of nitrogen in oxygen is unfavourable to the production of ozone, in consequence of the mutual action of ozone and peroxide of nitrogen. Indeed, they state that if a mixture of 1 part of nitrogen and 499 parts of oxygen be submitted to the action of a few large sparks of electricity, the mixture yields no ozone when subsequently submitted to a glow discharge. As under ordinary conditions the discharge in ozone generators of the Siemens type is apt to consist partly of rather large sparks which may not improbably lead to the production of peroxide of nitrogen,* it is evident that the complete absence of nitrogen is likely to be favourable to the production of ozone from oxygen in induction tubes.

b. The dryness of the oxygen, *and of the surfaces of the tubes* between which the discharge takes place, may affect the character of the discharge within it. In connection with this, the following observation will be interesting:—

In order to get an idea of the character of the electric discharge as it occurs in an ozone generator, we have repeated an experiment shown by one of us to the Physical Society in May, 1885. We fixed two strips of tinfoil, *a a*, of such dimensions that they correspond to the electrified surfaces of one of our most efficient ozone tubes, on the remote sides of sheets of patent plate glass *b b*, which are mounted on a small parallel vice, so that they can be made to recede from, and approach, each other (Fig. 6). The tinfoil is then connected with the wires from the coil, and the character of the discharge between the plates can be examined. When the glass plates are at a distance of a centimetre, the discharge between them consists of a few sparks, not very close together, corresponding in some degree to the spark discharge of the Rhumkorf coil, and it is by no means silent. If the plates are made to approach more closely, the number of these sparks increases till they become very numerous. When the distance approaches more nearly to that which we employ in the ozone generators, viz., 1 mm., we perceive, mixed with these sparks, what we may describe, for want of a better term, as a glow discharge, and if the plates be brought still a little closer, the discharge appears to consist of this glow almost entirely, with only a few of the larger sparks at considerable intervals. If now a little warm moist air be blown between the plates, the glow vanishes, the discharge is once more composed of comparatively few and large sparks. These are gradually replaced by the glow after the lapse of a few minutes. If, however, the discharge has been long passing between a pair of plates so that they have become warm, it is more difficult to obtain such startling contrasts, though it is not impossible to effect similar but less complete modifications of the discharge. We have also examined the discharge through oxygen. For this purpose, the plates *b b* were brought within a distance of 1 mm., and cemented at their edges with solid paraffin. Oxygen was conveyed to the flat vessel so obtained, and allowed to pass between the plates and escape at an opening left for that purpose, which also permitted us to observe the discharge within. The general character of the discharge corresponded with that of the discharge in air, but the glow discharge in oxygen seemed to us to present a somewhat washed-out appearance as compared with the glow discharge in air. From the considerable resemblance between the discharge which occurs between the two dry plates of glass when near to each other, and the glow discharge with which Andrews and Tait obtained such remarkable proportions of ozone from oxygen, and from the tendency of moisture on the plates to produce more or less the larger sparks which are known to destroy ozone when its amount exceeds certain narrow limits, we are inclined to consider that, at least to some extent, the high yield of ozone which appears to us to be produced by very dry oxygen, is due to the condition of the interior surfaces of the apparatus being exceedingly favourable to the occurrence of that form of electric discharge which would seem to be most efficient in effecting the conversion of oxygen into ozone.

---

* The results of an unpublished experiment by one of us confirms the idea that peroxide of nitrogen is sometimes formed in ozone generators.

In presenting these results, we would explain that we have made preparations for making other experiments of the same kind, more particularly with the object of gaining further information concerning the chemical activity of dry ozone, and concerning the efficiency of ozone generators of the type employed by Andrews and Tait, as compared with those of the Siemens form, which are now so generally employed. A long delay, however, must occur before these can be finished, and as we think the subject is one of considerable interest, we have not hesitated to bring forward by itself that portion of the work which is now completed.

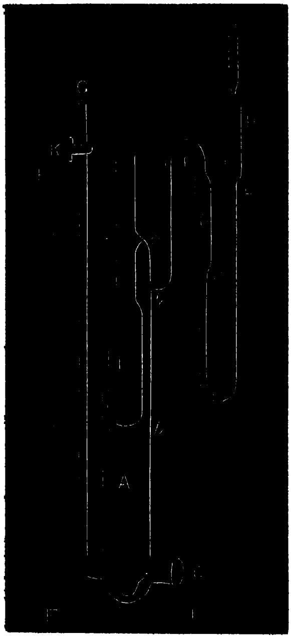
LIX.—*The Volumetric Relations of Ozone and Oxygen. A Lecture Experiment.*

By W. A. SHENSTONE and J. TUDOR CUNDALL.

SORET (*Ann. Chim. Phys.* [4], 7) showed that if it be true that ozone is completely absorbed by turpentine, then three volumes of oxygen are concerned in the production of two volumes of ozone. Subsequently Brodie re-examined this subject (*Phil. Trans.*, 1872) very carefully, and came to the same conclusion. And it has since been generally admitted by chemists that ozone is correctly represented by the formula O_3.

The operations of submitting a fixed quantity of oxygen to the action of the electric discharge and of turpentine in succession, and of observing the changes of volume which occur, are not very difficult and need not occupy much time. It has, therefore, occurred to us to construct an apparatus for the purpose of showing Soret's experiment to lecture classes (Fig. 1).

FIG. 1.



The tube B is united to A before the blowpipe at C, leaving an annular space between them. The distance of A from B may conveniently be about 1 mm. B is filled with dilute sulphuric acid, and tinfoil is wrapped round A between the dotted lines *h h*. A small bulb of turpentine is introduced into A through E, which is then closed by a cork. That part of the apparatus which comes within the area FFFF on the diagram is placed in a vessel of cold water. A current of oxygen is then sent through the arrangement, the oxygen being admitted at G and allowed to escape at H. A drop of strong sulphuric acid at I enables the operator to observe at what rate the current of oxygen passes. When the air has been displaced by oxygen, K is closed and sulphuric acid, coloured with indigo, is introduced into H. All this may be done by an assistant beforehand.

When the experiment is to be made, the level of the liquid in H is brought to L, a current of electricity is then passed through the annular space between A and B, by connecting the dilute sulphuric acid in B and the tinfoil on A with the electrodes of a Rhumkorf coil. A slight expansion occurs at first, which is quickly followed by a more or less rapid contraction. After a short while, the current of electricity is stopped, and when the subsequent contraction is complete, the new level of the liquid in H is observed. The bulb containing turpentine is then broken, after removing the apparatus from the water-bath, by submitting it to somewhat violent movements in a perpendicular direction, a stopper being held in H meanwhile, to avoid any risk of jerking the liquid from H. The apparatus is then returned to its bath and the absorption of the ozone by the turpentine is soon sufficiently complete. The experiment should be so conducted that the acid in O does not stand above P when the bulb of turpentine is broken, otherwise sulphuric acid may be thrown into A. This adjustment is readily made by holding the apparatus in the air of the room or near a lamp for a few moments, in order that the gas in A may expand slightly. Also, in order that the changes of level in the limb O may not introduce an error into the result, the liquid in O must stand at P at the beginning of the experiment.

We have used this apparatus several times with excellent results, and we think it will be a useful addition to the at present rather small number of *quantitative* lecture experiments at the command of chemists.

LX.—*The Action of Metallic Alkylates on Mixtures of Ethereal Salts with Alcohols.*

By T. Purdie, Ph.D., B.Sc., Professor of Chemistry in the University of St. Andrews.

In the course of an investigation of the action of sodic alkylates on ethereal fumarates and maleates (Trans., 1885, 855), I found that when a solution of sodic methoxide in methylic alcohol was added to ethylic fumarate, methylic fumarate was produced, and that a very small quantity of sodic methoxide sufficed to effect this change on a relatively large quantity of the ethereal salt.

In the communication referred to, I stated that the ethereal salts of cinnamic and oxalic acids, when treated in this manner, underwent similar changes, and that I had undertaken an investigation of the general reaction.

L. Claisen (*Ber.*, **20**, 646) has recently shown that the ethereal benzoates behave in a similar manner. Being desirous of reserving for myself the further investigation of at all events the special instances that have engaged my attention, I am induced, in view of Claisen's observations, to publish the results I have already obtained.

The experiments I have made show that the chemical change in question is a general one; that is to say, that when an alcohol is mixed with an ethereal salt containing a different alcoholic radicle from that of the alcohol, and to the mixture a small quantity of a metallic alkylate is added, a reaction takes place, which results in an extensive interchange of radicle between the ethereal salt and the alcohol; also, that the process possesses in a very marked degree the characteristic of continuous action.

The exchange of radicle occurring between the ethereal salt and the alcohol is most probably effected by the continuous formation and decomposition of an addition-compound, the derivative of an acid hydrol, which the ethereal salt forms with the alkylate. This explanation has been proposed by Armstrong and Groves (see *Miller's Elements of Chemistry*, III, Sec. I, 923) in the description of a closely allied reaction, and is applied by Claisen to the case of ethereal benzoates.

Conversion of Ethylic into Methylic Fumarate.

The phenomena attending the formation of methylic fumarate by the action of sodic methoxide on a mixture of the ethylic salt and methylic alcohol have been already described (*loc. cit.*, p. 859). The addition of ignited potassic carbonate produces the same effect as sodic methoxide; the carbonates of sodium and lithium, or ignited borax act in the same manner but more slowly. The effect of these reagents is probably due to the presence of small quantities of caustic alkali. Thus, 25 c.c. of some methylic alcohol which had been shaken up with potassic carbonate and filtered, and which contained in the 25 c.c. only 0·2 gram of solid matter, were added to 5 grams of ethylic fumarate; the mixture yielded 3 grams of dried crystals, which were found by their melting point (102°) and by analysis to be methylic fumarate.

	Calculated for $C_6H_8O_4$.	Found.
C	50·00	49·89
H	5·56	5·62

When, however, carbonic anhydride was passed through the methylic alcohol, treated as above, its action on the ethylic fumarate was very much retarded, the methylic fumarate making its appearance only after some days. The addition of the oxides of barium, calcium, lead or zinc, also effects the conversion of the ethylic into the methylic salt, the two latter oxides, however, acting very slowly. Calcium chloride, free from oxide and other neutral salts, produces no effect; a solution of zinc chloride in methylic alcohol, on the other hand, yields a precipitate of methylic fumarate, when the mixture with ethylic fumarate is allowed to stand a few days.

Conversion of Ethylic into Methylic Cinnamate.

Ethylic cinnamate and methylic alcohol do not act on each other at the ordinary temperature. When, however, a small quantity of sodic or potassic methoxide dissolved in methylic alcohol is added to a mixture of the two substances, the solution becomes yellow, and methylic cinnamate is formed, which may be separated by allowing the methylic alcohol to evaporate over sulphuric acid. The residual crystalline mass after being pressed in folds of filter-paper, dissolved in ether, filtered and again allowed to crystallise, yields pure methylic cinnamate, having the melting point 34°. Analysis gave the following numbers:—

	Found.	Calculated for $C_{10}H_{10}O_2$.
C	74·00	74·07
H	6·48	6·17

That the action of the alkylate is *continuous* is strikingly evident in the results of the following experiments, although the numbers given represent only approximately the actual extent of the chemical action, much of the methylic cinnamate being unavoidably lost in the process of freeing it from unaltered ethylic cinnamate.

(1.) 2 c.c. of a solution of sodic methoxide in methylic alcohol containing 0·1 gram of sodium were added to a mixture of 10 grams ethylic cinnamate, and 20 grams methylic alcohol, and the mixture allowed to stand at the ordinary temperature for some days, after which, on being treated as described above, it yielded 4·7 grams of nearly pure methylic cinnamate.

(2.) A mixture of 10 grams ethylic cinnamate, and 5 grams methylic alcohol to which 5 grams methylic alcohol containing 0·032 gram potassium hydrate were added, the whole being cooled by a freezing mixture to retard saponification, yielded 6·7 grams methylic cinnamate, mixed with the small quantity of potassium salt which was not separated from it.

(3.) 10 grams ethylic cinnamate, 20 grams methylic alcohol and 0·01 gram sodium, as methoxide, yielded 7·7 grams of dried crystals.

In experiments (2) and (3) the proportion of alkal-metal present amounts to less than 1 atom of metal to every 100 mols. of the ethereal salt employed, and yet the conversion into methylic cinnamate was almost quantitatively complete.

The addition of baric oxide, instead of the alkaline methoxide, also induces the formation of methylic cinnamate with production of baric cinnamate. An analysis of the salt gave 31·75 per cent. of barium instead of the calculated number 31·78.

Experiments with Ethereal Oxalates.

Ethylic Oxalate and Methylic Alcohol.—These substances do not act on each other at the ordinary temperature. When, however, a minute quantity of alkaline methoxide, dissolved in methylic alcohol, is added to the mixture, methylic oxalate is formed, and if the addition be made while the liquid is kept cool by means of a freezing mixture, an abundant crystallisation of methylic oxalate occurs at once. By evaporation over sulphuric acid in a vacuum and treatment with ether, as in the case of the corresponding cinnamate, the methylic oxalate is obtained pure. The substance prepared in this manner melted at 54°, and yielded the following results on analysis:—

	Found.		Calculated for
	I.	II.	$C_4H_6O_4$.
C	40·17	40·30	40·68
H	5·16	5·25	5·08

The results of the experiments, of which particulars are given below, show that varying the quantity of methylate within certain limits does not much affect the quantity of methylic oxalate produced, that much more, however, is produced when very small quantities of the methoxide are added, and that a very minute quantity of methoxide will convert almost the whole of the ethylic into methylic oxalate if the experiment is conducted at a low temperature. 20 grams ethylic oxalate and 45 grams methylic alcohol were used in each experiment, and the alkaline reagents were added in solution in a part of the alcohol.

Experiment.	Alkaline reagent employed.	No. of atoms, K or Na, to 100 mols. ether.	Yield of methyl oxalate.
1	3·04 grams KOH	40	4·36 grams.
2	1·52 " "	20	4 18 "
3	0·76 " "	10	5·50 "
4	0·38 " "	5	5·37 "
5	0·38 " "	5	11·60 "
6	0·27 " "	5	10·50 "
7	0·27 " "	5	11·70 "
8	0·02 " "	0·6	13·00 "

In experiments 5, 7, and 8, a freezing mixture was used.

The potassium salt produced was potassic methylic oxalate. It gave on analysis 27·23 per cent. of potassium instead of the calculated number 27·52. The formation of this salt by the action of potassic methoxide on ethylic oxalate was observed by Salomon (*Ber.*, **8**, 1506).

Methylic Oxalate and Ethylic Alcohol.—To a mixture of 10 grams methylic oxalate and 26 grams ethylic alcohol, cooled in a freezing mixture, 0·03 gram sodium as ethoxide was added. The mixture was evaporated over sulphuric acid in a vacuum. The crystals of methylic oxalate were found to have diminished in quantity; they were covered with an oil which did not evaporate, and which boiled at 180—190°. The boiling point of ethylic oxalate is 186°. The residual crystals, found by their melting point to be unchanged methylic oxalate, weighed when dried 4·6 grams. A blank experiment performed with the same quantities of material, excluding the sodium ethoxide, left no oil on evaporation, and the residual methylic oxalate weighed 9 grams.

It appears, therefore, that on the addition of methylic alkylate, methylic oxalate and ethylic alcohol act on each other in the same manner as ethylic oxalate and methylic alcohol.

In the following experiments with ethereal oxalates, fractional distillation had to be resorted to, which might readily cause an interchange of alcoholic radicle between the ethereal salt and the alcohol, by direct double decomposition. Accordingly, for the purpose of comparison, a blank experiment was performed in each case, the quantities of materials, excluding the alkylate, and other conditions being the same as in the actual experiment.

Amylic Oxalate and Ethylic Alcohol.—The blank experiment showed that when a mixture of these substances in the proportion of 1 mol. oxalate to 4 mols. alcohol is subjected to distillation, little change takes place. After the ethylic alcohol was distilled off the thermometer rose rapidly to 260°, the boiling point of amylic oxalate. A similar mixture, to which sodium ethoxide in the proportion of 1 atom of sodium to 100 mols. oxalate was added, yielded, contrary to expectation, no ethylic oxalate, though the production of a little amylic alcohol and the gradual rise of the thermometer from 140° to 260° indicated that probably some ethylic amylic oxalate had been formed.

Ethylic Oxalate and Amylic Alcohol.—A mixture in the proportion of 1 mol. ethereal salt to 4 mols. alcohol underwent little or no chemical change on distillation. On distilling a similar mixture to which sodium, as amyl oxide, was added in the proportion of about 1 atom of sodium to 50 mols. of ethereal salt, it was found that a great interchange of alcoholic radicle had taken place. Thus 60 grams ethylic oxalate, 145 grams amylic alcohol, and 0·18 gram sodium yielded only 4·5 grams distillate between 150° and 200°, the ethylic oxalate (b. p. 186°) having almost entirely disappeared, while ethylic alcohol, amylic oxalate, and, apparently, ethylic amylic oxalate, had been produced. The latter product, however, did not separate distinctly from the higher and lower fractions, and probably underwent decomposition on boiling (Friedel and Crafts, *Annalen*, **130**, 201).

Amylic Oxalate and Methylic Alcohol.—These substances, when mixed in the same proportions as in the two preceding experiments, distil almost unchanged—not a drop of liquid passing into the receiver between 100° and the boiling point of amylic oxalate. A mixture to which sodium methoxide was added, gave distinct evidence of interchange of alcoholic radicle, though, as in the case of the corresponding reaction between amylic oxalate and ethylic alcohol, the interchange was much less extensive than in the reverse reaction between ethylic oxalate and amylic alcohol. A mixture consisting of 30 grams amylic oxalate and 17 grams methylic alcohol, to which 0·03 gram sodium, as methoxide, was added, yielded 8·8 grams distillate between 220° and 260°, the latter being the boiling point of amylic oxalate, and from the lower boiling fractions 2·2 grams of the crystalline methyl oxalate (m. p. 54°) was obtained.

Experiments with Ethereal Acetates.

In these experiments the various mixtures were prepared as follows:—The sodium, potassium, or potassic hydrate being dissolved in a portion of the alcohol—usually the half of it—the solution was added slowly to the mixture of the ethereal salt with the rest of the alcohol, while the liquids were kept cool by means of freezing materials. After standing at least 24 hours, the mixtures were fractionally distilled, the distillation being repeated three times. The distillation was not carried further than this, as it would have involved proportional loss of material without effecting complete separation of the alcohols and ethers present. The fraction containing the ethereal salt formed by the reaction was saponified with an excess of standard solution of potassic hydrate, the liquid made up to a convenient volume, and the free alkali determined by titration with standard sulphuric acid. From the amount of potassic hydrate consumed in the hydrolysis, the percentage of the ethereal salt used, which had undergone a change of alcoholic radicle, was calculated.

The numbers obtained in the manner described can evidently be regarded only as approximate values; besides the error due to imperfect separation of the ethers, portions of them were lost owing to the difficulty of distilling off the liquid to dryness from the residual alkaline salt.

In the blank experiments, the distillation and hydrolysis were carried out under the same conditions as in the corresponding experiments to which the alkylate was added.

Amylic Acetate and Ethylic Alcohol.—The results given below were obtained by the hydrolysis of the fractions boiling under 90°.

	Employed.				Percentage amylic acetate converted.	
	Amylic acetate.	Ethylic alcohol.	Sodium or potassium.	No. of atoms, K or Na, to 100 mols. acetate.	Experiment with alkylate.	Experiment without alkylate.
	grams.	grams.	gram.		per cent.	per cent.
1	50	72	0·75 K	5	61·8	16·5
2	50	36	0·15 „	1	39·7	6·8
3	50	36	0·44 Na	5	45·6	
4	50	36	0·08 „	1	38·5	

The results of these experiments exhibit in a striking manner the effect produced by small quantities of alkylate. Experiments 3 and

4 show the effect of varying the quantity of the ethylate, 1 and 2 the influence of the proportion of alcohol present. In 1 and 2, the proportions are respectively 4 and 2 mols. alcohol to 1 mol. of the ethereal salt. Experiments 2 and 4 indicate that equivalent quantities of potassium and sodium have much the same effect.

Ethylic Acetate and Amylic Alcohol.—50 grams of ethylic acetate, 100 grams of amylic alcohol, and 0 65 gram of sodium were used, the proportions being 200 mols. of alcohol and 5 atoms of sodium to 100 mols. ethereal salt. The formation of amylic acetate was indicated by the results of distillation, a considerable portion of the liquid boiling at 130—135°, while in the case of the blank experiment all passed over under 130°. The fraction 120—135°, and in the blank experiment the fraction 120—130°, were saponified with standard alcoholic solution of potassic hydrate.

In the experiment to which the alkyl oxide was added, 44·7 per cent. of the ethylic acetate used was converted into amylic acetate, while in the blank experiment only 6·7 per cent. was so converted.

Amylic Acetate and Methylic Alcohol.—50 grams of amylic acetate, 25 grams of methylic alcohol, and 0·44 gram of sodium were employed, the molecular proportions being the same as in the last experiment. The portions boiling under 80° were saponified. In the experiment with methoxide, 55·8 per cent. of the amylic acetate was converted into methylic acetate, whilst in the experiment without the methoxide only 2·6 per cent. was converted.

Phenylic Acetate and Ethylic Alcohol.—A mixture of 50 grams of phenylic acetate, 40 grams of ethylic alcohol, and 2 grams of potassic hydrate was allowed to stand for a fortnight, by which time the liquid had turned of a dark-brown colour. It was shaken up repeatedly with a saturated solution of common salt; the supernatant oil being separated, dried, and subjected to fractional distillation, yielded 23·6 grams of nearly pure phenol boiling at 180—183°, scarcely any phenylic acetate being left unacted on, while from the lowest boiling fraction, after repeated washing with a saturated solution of salt, 17 grams of approximately pure ethylic acetate (b. p. 73—76°) were obtained. An analysis gave 53·97 per cent. of carbon and 9·53 per cent. of hydrogen instead of 54·54 and 9·09 per cent. An experiment similarly conducted with 30 grams of phenylic acetate, in which no potassic hydrate was used, yielded only 2 grams of ethylic acetate, and so little phenol that it did not separate in the solid state from the unaltered phenylic acetate.

A mixture of 35 grams of phenylic acetate with an equal weight of ethylic alcohol and 0 7 gram potassic hydrate was left two or three days and then fractionally distilled. By saponifying the fraction boiling under 100°, it was found that 69·4 per cent. of the phenylic acetate had been converted into the ethylic salt, while in a blank experiment only 12·7 per cent. was thus converted.

It may be concluded that the reaction, of which a number of illustrations has been given, is of general application, and embraces within its scope, besides the case of the benzoic ethers observed by Claison, various isolated reactions described by different investigators, such as the action of sodium and potassium alkylates on ethereal thiocarbonates (*Ber.*, **8**, 1506), and on mixtures of ethereal acetoacetates, and of ethereal propiopropionates with alcohols (*Annalen*, **231**, 229, and **234**, 262); also the action of ethyl alcoholic ammonia on methylic oxalate (*J. pr. Chem.* [2], **12**, 434).

I purpose making a more thorough investigation of the reaction in the case of the ethereal salts of fumaric, cinnamic, and oxalic acids, with the view of elucidating the properties of the derivatives of the acid hydrols through the agency of which the reaction probably takes place.

LXI.—*On Phlorizin.*

By EDWARD H. RENNIE, M.A., D.Sc., Professor of Chemistry in the University of Adelaide, South Australia.

IN a paper on "Glycyphyllin, the Sweet Principle of *Smilax Glycyphylla*," communicated to the Society some few months ago (Trans., 1886, 857), it was suggested as possible, though scarcely probable, that this substance might be identical with phlorizin. The idea of such a possibility arose out of the following considerations:—

1. Glycyphyllin yields phloretin and isodulcite on hydrolysis, whereas phlorizin yields phloretin and a sugar about which some uncertainty has hitherto existed; Hesse maintaining (*Miller's Chemistry*, 5th Edition, Part III, 582) for reasons to be hereafter mentioned, that it is *not* identical with ordinary dextrose. Moreover, isodulcite has apparently been more than once mistaken for dextrose. (See Will, *Ber.*, **18**, 1312.)

2. Considerable discrepancies are noticeable in the published analysis of phlorizin, so much so that the generally accepted formula of Stas, $C_{21}H_{24}O_{10}$, has been called in question by Loewe (*Watts' Dictionary*, 8, Part II, p. 1569), who proposes another formula and another equation to represent its hydrolysis. His results, however, as is pointed out (*loc. cit.*), do not harmonise well with known

facts. Hugo Schiff also (*Ber.*, **14**, 303) has drawn attention to the want of agreement in the published analyses of phlorizin.

Under these circumstances, it seemed worth while to re-examine this substance, and to that end a specimen obtained from Trommsdorff was twice recrystallised and then analysed.

Results of Analysis.

The following are the results in brief of four analyses of the anhydrous substance:—

	Theory for $C_{21}H_{24}O_{10}$.	Found.			
		I.	II.	III.	IV.
Carbon ..	57·79	57·03	57·11	57·15	57·17
Hydrogen.	5·50	5·89	5·91	5·67	5·70
Oxygen ..	36·71	—	—	—	—
	100·00				

Though these numbers are not very far from those indicated by theory for the above formula, they are scarcely satisfactory. A fresh specimen was therefore prepared by repeated crystallisation from water. The substance so obtained consisted of perfectly white, well-defined, silky needles; it was analysed without dehydration, having been previously thoroughly air-dried. It contained 7·58 per cent. of water of crystallisation, the theory for 2 mols. H_2O requiring 7·62 per cent. The following are the results:—

	Substance.	CO_2.	H_2O.
I	0·3202	0·6217	0·1792
II	0·3109	0·6065	0·1728

	Calculated for $C_{21}H_{24}O_{10},2H_2O$.		I.	II.
C_{21}	252	53·39	52·95	53·20
H_{28}	28	5·93	6·21	6·17
O_{12}	192	40·68	—	—
	472	100·00		

These number are much more satisfactory and confirm the original analyses and formula of Stas.

Decomposition by Dilute Sulphuric Acid.

It being impossible to refer to the original papers here in Adelaide, it has not been possible to ascertain whether any quantitative experiments have been made to determine the amounts of phloretin and sugar, respectively, yielded by the hydrolysis of phlorizin. Two experiments were therefore made, the method used being practically the same as that described in the case of glycyphyllin (Trans., 1886, 864), except that the main portion of the phloretin was weighed on a filter-paper of known weight. The results of the titration of the filtrate were of course calculated on the assumption that the sugar is dextrose.

The following were the numbers obtained:—

Anhydrous substance.	Phloretin.	Dextrose.
2·2980	1·4375	0 9671
3·3114	2·0729	1·3514

	Calculated for hitherto assumed equation.	Found. I.	Found. II.
Phloretin	62·82 per cent.	62·55	62·59
Dextrose	41·28 ,,	42·09	40·80

These numbers are sufficiently near to those required by the hitherto assumed equation—

$$C_{21}H_{24}O_{10} + H_2O = C_{15}H_{14}O_5 + C_6H_{12}O_6,$$

to afford strong confirmation of its truth. It may be noted here that the equation by which Loewe (*Watts' Dictionary*, 8, Part II, p. 1570) represents the decomposition of phorizin, requires 63·5 per cent. phloretin and only 36·4 per cent. dextrose, reckoned on the anhydrous substance.

Examination of the Sugar obtained.

The filtrate from the decomposition (by dilute sulphuric acid) of a considerable quantity of phlorizin was neutralised by barium carbonate, filtered and concentrated over a water-bath. A good deal of colouring matter formed. This was removed by repeated treatment with animal charcoal, and the solution finally concentrated to a syrup in a vacuum, over sulphuric acid. On adding a small quantity of water to this syrup, and allowing it to stand for a few days exposed to the air, it gradually became an almost solid mass of minute, perfectly white crystals. These were dried on the filter-pump, washed two or three times with a small quantity of water, and finally spread out to dry in the air.

According to Hesse (*Miller's Chemistry*, 5th Edition, Part III, p. 582) the sugar from phlorizin differs from dextrose in the following particulars:—

1. The melting point of the hydrated crystals is 74°, that of dextrose being 82° according to Hesse (*Annalen*, **176**, 103), or 86° according to Schmidt (*Annalen*, **119**, 92).

2. It loses only 6·7 per cent. of water at 60—70°, and requires a temperature of 105° to expel the last traces of water.

3. The specific rotatory power (sodium light) after standing, is 44°, that of dextrose according to various observations ranging from about 53° to 57·6° for solutions containing 10 per cent., or thereabouts, of anhydrous glucose.

With reference to the second point, there seems to be some difference of opinion as to the temperature at which dextrose becomes anhydrous. In the latest edition of Beilstein's *Handbuch der organischen Chemie* is the following statement: "Krystallisirter Traubenzucker verliert das Krystallwasser unter 100° unter Schmelzung und ist bei 110° wasserfrei," apparently implying that a temperature of 110° is required to remove the last traces of water.

The sugar under examination melted at 85—86° when carefully heated in a capillary tube. Heated at 100°, it lost 8·64 per cent. of its water: theory for 1 mol. H_2O indicating 9·09 per cent. Heated at 102—103°, the loss increased to 9·32 per cent.

A solution was made containing 10·204 grams anhydrous substance in 100 c.c.* This, after standing, gave a rotation of 11·83° in a tube 200 mm. in length, the observations being made with a Laurent's polarimeter using sodium light. This gives—

$$[\alpha]_D = \frac{11{\cdot}83^\circ}{2 \times 0{\cdot}10204} = 57{\cdot}9^\circ.$$

Finally, a solution, when treated with phenylhydrazine hydrochloride in the manner recommended by Fischer (*Ber.*, **17**, 579), yielded a yellow, crystalline precipitate exactly corresponding with that described as given by dextrose, and with a melting point 204—205°, when heated in a capillary tube. The facts above adduced leave little doubt that the statements generally made as to the formula and hydrolysis of phlorizin are correct, and that the sugar yielded by it is really dextrose.

---

* It was intended to make this solution by dissolving a weighed quantity of the crystals in 100 c.c. water, but an accident having happened to the solution in course of preparation, and no more substance being available, the strength was carefully determined (after dilution) by titration with Fehling's solution.

LXII.—*Further Notes on the Chemical Action of* Bacterium Aceti.

By ADRIAN J. BROWN.

IN my previous paper on the chemical action of *Bacterium aceti* (Trans., 1886, 172), I described the oxidising action of the pure ferment on mannitol, showing that this carbohydrate is completely decomposed, and that a sugar, lævulose, is the main product formed from it.

As dulcitol is an isomeride of mannitol, it appeared interesting to ascertain if *B. aceti* had any action on it, more especially as, according to Carlet (*Compt. rend.*, 51, 137), dulcitol yields a $C_6H_{12}O_6$ sugar on oxidation with dilute nitric acid; Fudakowski (*Chem. Centr.*, 1887, 5) also obtaining a sugar from it by oxidation with potassium permanganate. Solutions of dulcitol in yeast-water were therefore prepared in a similar manner to those of mannitol described in my previous paper, and after inoculation with *B. aceti*, the ferment was allowed to grow in them for from two to four months. In no case, however, although the ferment grew freely, could the least action on the dissolved dulcitol be detected, and the dulcitol was recovered from the solutions unaltered. It is evident, therefore, that dulcitol is not susceptible to oxidation by means of *B. aceti*, differing in this respect very markedly from its isomeride mannitol.

Action of B. Aceti *on Glycol.*

The action of *B. aceti* on the dihydric alcohol, glycol, was next studied. A 2 per cent. solution of this alcohol in yeast-water was sterilised and inoculated with the ferment in the usual manner. At first, the ferment grew freely, forming a pellicle on the surface of the liquid. This growth, however, appeared to be speedily checked, and in five weeks' time all action was evidently over. On opening the flask, the solution was found to be slightly, but distinctly, acid: a portion was evaporated to a small bulk and filtered, and the absence of any acid giving an insoluble lime salt proved.

The rest of the solution was boiled with calcic carbonate, filtered, and the lime salt so formed precipitated by excess of alcohol. The precipitate was redissolved and reprecipitated several times, until it came down in colourless flocks, which were dried at 100° and weighed, giving 0·0533 gram of substance. A determination of the lime in this small precipitate was then made, showing it to contain 28·90 per cent. CaO. As glycollate of calcium contains 29·47 per cent. CaO, it appeared very probable that the small amount of acid formed from glycol during the experiment was glycollic acid, and that a small percentage of this acid in solution checked the further action of the ferment in a manner similar to that of gluconic acid in the fermentation of dextrose in acid solution.

A second experiment was therefore made with a 2 per cent. solution of glycol in yeast-water, but also containing a large excess of calcic carbonate to neutralise the acid when formed. After inoculation, the ferment grew very freely, and the calcic carbonate dissolved quickly. In two months' time, when all action had ceased, the flask was opened, and the solution filtered, and evaporated to a small bulk. Concretions of minute needle-shaped crystals quickly formed on cooling the concentrated liquid, and these were purified by recrystallisation from water several times, until a pure white mass of crystals was obtained. After drying a portion of these at 110°, 0·2535 gram was treated with sulphuric acid and ignited, yielding 0·1808 gram calcic sulphate. This gives 29·36 per cent. CaO in the original salt; calcic glycollate containing 29·47 per cent. CaO. The air-dried crystals of the salt were found to contain 2 mols. H_2O, the amount found in crystals of calcic glycollate; the crystalline form of both salts is also similar. There is no doubt therefore that the salt obtained is calcic glycollate, and therefore that glycollic acid is formed by the action of *B. aceti* on glycol under the circumstances described above. No indications of the formation of any compound besides glycollic acid were observed, so that probably the action of the ferment may be represented simply thus:—

$$CH_2(OH){\cdot}CH_2(OH) + O_2 = CH_2(OH){\cdot}COOH + OH_2.$$

Action of B. Aceti *on Glycerol.*

The action of *B. aceti* on the dihydric alcohol, glycol, having been studied, similar experiments with the trihydric alcohol, glycerol, naturally suggested themselves.

The first experiment was made with a 5 per cent. solution of pure glycerol in yeast-water, in which the ferment was allowed to grow under the usual circumstances frequently mentioned before. From the first, the bacteria increased with remarkable freedom, and after the expiration of 11 weeks, when the flask was opened, there appeared to be a larger growth of the ferment, both in the liquid and as a deposit at the bottom, than I had previously observed in any other experiment with *B. aceti*. At intervals during the fermentation of the solution, portions of liquid were withdrawn with a sterilised pipette, and tested for acid. Although the first of these samples, withdrawn from the solution shortly after the commencement of the fermentation, showed that a very small amount of free acid was present, yet, although the ferment was still continuing to grow with great vigour, the subsequent samples withdrawn showed little, if any, increase in the amount of this acidity. At the end of the experiment, titration of a portion of the solution showed that there was 0·114 per cent. acid present calculated as acetic acid. On distilling the rest of the solution, no acid or other volatile product passed over. An attempt was then made to determine the nature of the acid in the residue by saturating it with baric carbonate, and precipitating the filtered solution by alcohol. The small flocculent precipitate of impure baric salt obtained was redissolved in water and reprecipitated by alcohol several times. The very small amount of salt thus obtained (about 50 mgrms.) was, however, still so impure that a barium determination could not have afforded any satisfactory evidence as to its composition.

A second experiment was made in which 10 grams of glycerol dissolved in 400 c.c. yeast-water, with 2 grams calcic carbonate added, was acted on by *B. aceti* for nine weeks. In this experiment, the ferment grew with even greater freedom than in the first one. During the fermentation, the calcic carbonate, lying at the bottom of the flask in a thin layer, was observed carefully, but the amount dissolved by the solution was so slight as not to be appreciable. At the close of the experiment, when the fermentation had come to an end, the solution was filtered, and evaporated gently on a water-bath. The residue was then thoroughly exhausted with absolute alcohol, to extract glycerol from it, and the solution thus obtained was evaporated, and again exhausted with alcohol and ether. This solution, which should contain all the glycerol present in the original liquid, was then evaporated and the residue weighed. The weight of this residue was, however, only 0·0492 gram of a resinous substance in which no indications of glycerol could be detected. Thus, the action of *B. aceti* on the 10 grams of glycerol originally taken had decomposed the whole of it.

The residue left after exhaustion with absolute alcohol was dissolved in a little water, and the small amount of lime salt it contained was precipitated by alcohol. The precipitate so obtained was purified as far as possible by alternate solution in water and reprecipitation by alcohol, and the aqueous solution finally left to evaporate at the ordinary temperature. No crystals were formed however, only a clear, yellowish, vitreous mass being left. The total weight of th salt dried at 100° was 0·2050 gram. After drying at 115°, 0·1495 gram of the substance yielded 0·0690 gram calcic sulphate, which corresponds to 19 per cent. CaO in the original salt. Calcic glycerate, the most likely salt to be found under the above circumstances, contains 22·40 per cent. CaO; if therefore the compound with which we are dealing is really calcic glycerate, the separation of the small amount of salt formed from other salts and impurities in the mother-liquid, has been incomplete. I have made several attempts to prepare this acid in larger quantities, but have failed, the quantity of acid never appearing to increase beyond a certain small amount.

It appears from the above experiments, therefore, that the action of *B. aceti* on glycerol is to decompose it into carbonic acid and water, the only other product of the action being a very small amount of an acid the nature of which is undetermined. It is possible that this acid may be due to a slight and undetected impurity in the original glycerol used, but I have been unable to carry these experiments further at present.

Glycerol seems to favour the growth of *B. aceti* better than any other substance with which I have experimented.

Action of B. Aceti *on Erythrol.*

Solutions of this tetrahydric alcohol in yeast-water, both with and without calcic carbonate, were submitted to the action of *B. aceti*, but although the ferment grew freely, no action on the erythrol could be detected; nearly the whole of the substance used was recovered by crystallisation from the original solutions, although it had been under the influence of *B. aceti* for 12 weeks.

The fact that erythrol is not acted on by *B. aceti* is interesting, because this same substance is oxidised by platinum-black to erythric acid. The non-activity of *B. aceti* on methyl alcohol, described in my previous paper (Trans., 1886, 177), is another case in which the action of this ferment differs entirely from the activity of platinum-black. It had been suggested by several writers that the mode of action of platinum-black is similar to that of *B. aceti*, from the similarity in the action of both on ethylic alcohol. I consider this idea doubtful, for although it is quite true that in the greater number of experiments which I have described where *B. aceti* has had an oxidising action, the compound is also oxidised by platinum-black, as in the cases of mannitol, glycol, and glycerol; yet the results of these reactions usually differ, so far as we know. For instance, in the action of platinum-black on mannitol, according to Gorup-Besanez (*Annalen*, **118**, 273), two of the chief products formed are an acid, mannitic acid, and a sugar not affecting polarised light. Now, in the action of *B. aceti* on mannitol, we have no acid at all formed, and a sugar, lævulose, having a very strong lævorotatory power on polarised light. Again, according to Döbereiner (*J. pr. Chem.*, **29**, 453), an aqueous solution of dextrose in contact with platinum-black, does not absorb oxygen until caustic potash is added, when it is oxidised to carbonic acid and water; but *B. aceti* acts freely on dextrose in neutral solutions, gluconic acid being formed.

It will be noticed, therefore, that not only is *B. aceti* unable in some cases to oxidise a compound which is oxidised by platinum-black, but also, that in the action of the ferment and of platinum-black on the same compound, the products formed in these actions usually differ. It seems most probable then, in the case of ethylic alcohol, on which both *B. aceti* and platinum-black act, yielding similar products, that the generally assumed similarity of mode of action is incorrect, the resemblance of the two actions being merely accidental.

In my previous paper on *B. aceti*, after describing the conversion of mannitol into lævulose by this ferment, I stated that we had means here of converting dextrose into lævulose by first transforming the dextrose into mannitol by means of sodium amalgam, "always supposing that the mannitol so formed is identical with that from manna." Since writing the above, I have prepared mannitol by the sodium amalgam method, with a view of testing this identity.

The dextrose used in the preparation of the mannitol was carefully recrystallised from the sugar formed by the action of acid on starch, thus avoiding any danger of contamination with lævulose. Dewar's method (*Phil. Mag.*, 4, 39) was followed in the conversion of the dextrose by sodium amalgam. When the reaction was complete, the hot alcoholic extract of the residue left on evaporation of the original solution was put on one side for the mannitol formed to crystallise out, this, however, not taking place until it had been standing for six weeks * The total weight of crystallised mannitol thus obtained only slightly exceeded 7 per cent. of the original dextrose taken. After purification by repeated recrystallisation from alcohol, the melting point of the crystals was compared with that of mannitol from manna, the actual numbers found being 164° for the former, and 165° for the latter (a sample of mannitol prepared from lævulose melting at 166°). Microscopic examination of all three samples showed that their crystalline forms were also similar.

The sample of mannitol prepared from dextrose was then submitted to the action of *B. aceti*. After the action of the ferment was over, lævulose was found in the solution, thus completing the conversion of dextrose into lævulose. There can be but little doubt, therefore, that the mannitol formed by the action of sodium amalgam on dextrose is identical with that prepared from manna.

---

* This length of time in crystallising will probably account for the doubt that has been expressed by some writers as to the real conversion of dextrose into mannitol.

Note on the Cellulose formed by Bacterium Xylinum.

By Adrian J. Brown.

In a previous paper, I described an acetic ferment, *B. xylinum* (Trans., 1886, 432), which had the peculiar property of converting both dextrose and lævulose into cellulose.

It has since been suggested to me that it would be interesting to ascertain whether cellulose formed by the ferment from lævulose would yield a dextrorotary sugar on treatment with sulphuric acid like ordinary cellulose, or whether a lævorotary sugar would be formed.

In order to ascertain this, a membrane of the ferment was grown in a yeast-water solution of lævulose prepared from pure inulin. Additional evidence that dextrose was not present in the lævulose used was afforded by the fact that the solution remained quite neutral after the growth of the ferment; if dextrose had been present, the solution would have become acid from the formation of gluconic acid. The membrane of the ferment developed was then treated in the way described in my previous paper, until pure cellulose was obtained from it. This cellulose after drying at 100° was then dissolved in strong sulphuric acid, diluted with water, and boiled. After getting rid of the excess of sulphuric acid by baric carbonate, the filtered solution was concentrated by evaporation and again filtered from a further deposit of baric carbonate.

The solution thus obtained was found to have a strong dextrorotary action on polarised light and a strong cupric oxide reducing power, the solution being also fermentable. The relation of the rotary power to the cupric oxide reducing power approximated to that of dextrose; the small amount of material at command did not admit, however, of tracing the character of the sugar more closely than this.

It appears then that cellulose formed from lævulose by *B. xylinum*, yields a dextrorotary sugar on hydrolysis in a similar manner to ordinary cellulose, and a way of converting a lævo- into a dextrorotary sugar is thus shown.

LXIII.—*The Composition of Prussian Blue and Turnbull's Blue.*

By Edgar J. Reynolds, Student in the Laboratory of the Normal School of Science, Science and Art Department.

We are indebted to Dr. Williamson for the most satisfactory preparation and analyses of these two compounds. On his authority, the two substances are generally regarded as dissimilar in composition, and are respectively designated by the formulæ Fe_7Cy_{18} and Fe_5Cy_{12} (*Mem. Chem. Soc.*, **3**, 125). It has, however, been conjectured by Reindel (*J. pr. Chem.*, **102**, 38) and others that these two compounds are identical. This view has been based on the oxidising power of ferricyanide of potassium on the one hand and the reducing power of ferrocyanide of potassium on the other, either of which might account for the supposed identity in composition.

Thus, we might have—

$$\begin{aligned}2K_3Fe'''Cy_6 + 3FeCl_2 + H_2O &= 2HK_3Fe''Cy_6 + FeO + Fe_2Cl_6\\ &= Fe'''_2Fe''(Fe''Cy_6)_3 + H_2O + 6KCl,\end{aligned}$$

$$\text{and}\left\{\begin{aligned}&2K_4Fe''Cy_6 + Fe_2Cl_6 = Fe'''_2K_2(Fe''Cy_6)_2 + 6KCl\\ &Fe'''_2K_2(Fe''Cy_6)_2 + FeCl_2 = Fe'''_2Fe''(Fe''Cy_6)_2 + 2KCl,\end{aligned}\right.$$

while, on the other hand—

$$\begin{aligned}2K_4Fe''Cy_6 + Fe_2Cl_6 + FeCl_2 &= 2K_3Fe'''Cy_6 + 3FeCl_2 + 2KCl\\ &= Fe''_3(Fe'''Cy_6)_2 + 8KCl,\end{aligned}$$

the action of the ferrous salt on the ferricyanide being a case of double decomposition.

Skraup has shown (*Annalen*, **186**, 371) that soluble Prussian blue, $Fe'''_2K_2(Fe''Cy_6)_3$, may be prepared either by the action of a ferrous salt on ferricyanide of potassium or by the action of a ferric salt on ferrocyanide of potassium, and that the two compounds so obtained are identical. He also states that by the action of a ferrous salt on this compound (soluble blue), Turnbull's blue, Fe_5Cy_{12}, is obtained, and by the action of a ferric salt Prussian blue, Fe_7Cy_{18}, is produced. But with regard to the latter, the analysis he gives, though nearer the formula Fe_7Cy_{18} than Fe_5Cy_{12}, is yet so different as to be almost valueless. Thus he finds a percentage of Fe = 32·85 per cent., of C = 20·33 per cent. This gives the ratio of Fe : C as 1·61 : 1—whereas the formula Fe_7Cy_{18} demands 1·81 : 1. He further states that whether the compound Fe_5Cy_{12} or Fe_7Cy_{18}, is formed in the manufacture of Prussian blue depends entirely on the amount of oxidising agents present. Skraup also studied the conditions under which oxidation and reduction respectively took place when the double cyanides of iron and potassium were mixed with iron oxides (or hydrates). He found that ferric hydrate was speedily reduced by ferrocyanide of potassium to ferroso-ferric hydrate at the ordinary temperature. If, therefore, a corresponding reduction takes place when an iron salt is used instead of the hydrate—we should have a mixture of ferric and ferrous salts which would be in the proportion necessary (according to the equations already given). It was therefore of interest to see whether or no these two compounds would prove to be identical when prepared under like conditions, and when all precautions were taken to prevent oxidation. The method adopted was as follows: Prussian blue was made by the action of ferric chloride on hydroferrocyanic acid. The acid was prepared by the action of dilute sulphuric acid on lead ferrocyanide, as by this means the whole experiment of making the Prussian blue could be effected at one operation. The water in which the lead ferrocyanide was suspended had by long-continued boiling been freed from air, and the dilute acid was also similarly freed from air. The experiment was conducted in an atmosphere of carbon dioxide, and carried on in the cold throughout. The precipitate of Prussian blue, after being washed by decantation, was thrown on to a filter, thoroughly washed, and then dried over sulphuric acid in a vacuum. The substance was tested, and found to be quite free from alkali. Analyses gave the following results:—

I.	0·3838 gram gave	0·2773 CO_2	= 19·71	per cent.	C.
	0·3857 „ „	0·2797 CO_2	= 19·78	„	C.
	0·7695 „ „	0·3915 Fe_2O_3	= 35·63	„	Fe.

This gives ratio of Fe to C as 1·80 : 1.

II.	0·3563 gram gave	0·2574 CO_2	= 19·70	per cent.	C.
	0·3583 „ „	0·2583 CO_2	= 19·66	„	C.
	0·7146 „ „	0·3654 Fe_2O_3	= 35·79	„	Fe.

This gives ratio of Fe to C as 1·82 : 1.

Taking the mean of these analyses, we get the ratio of Fe : C as 1·81 : 1, which is exactly what is required by the formula Fe_7Cy_{18}. (I) and (II) were from the same preparation, but in slightly different states of hydration.

Turnbull's blue was prepared in a manner exactly similar by acting on ferrous sulphate with hydroferricyanic acid. The acid was prepared from lead ferricyanide by decomposing a saturated solution of it with sulphuric acid. Precisely similar precautions were taken as in the case of Prussian blue. Analysis showed—

I.	0·3553 gram gave	0·2349 CO_2	= 18·00	per cent.	C.
	0·3540 „ „	0·2347 CO_2	= 18·01	„	C.
	0·7093 „ „	0·3505 Fe_2O_3	= 34·59	„	Fe.

This gives the proportion of Fe to C as 1·92 : 1.

$$\text{II.}\begin{cases}0\cdot3286 \text{ gram gave } 0\cdot2160\ CO_2 = 17\cdot93 \text{ per cent. C.}\\ 0\cdot3334 \quad ,, \quad ,, \quad 0\cdot2190\ CO_2 = 17\cdot91 \quad ,, \quad \text{C.}\\ 0\cdot6620 \quad ,, \quad ,, \quad 0\cdot3267\ Fe_2O_3 = 34\cdot54 \quad ,, \quad \text{Fe.}\end{cases}$$

This gives the ratio of Fe : C as 1·93 : 1.

Taking the mean result, we get the ratio of Fe to C as 1·93 : 1. The ratio required for the formula Fe_5Cy_{12} is 1·94 : 1.

(I) and (II) were not exactly in the same state of hydration.

These results, then, clearly show that the formulæ given by Williamson are correct, and that the two blues are not identical in composition. The water present in the compound has not been included in the formula, because no particular stage of hydration was accompanied by any characteristic physical properties. In well-dried samples, the amount in Prussian blue was about 22 per cent., corresponding approximately with the formula $Fe_7Cy_{18},14H_2O$; in Turnbull's blue about 26 per cent., corresponding with about $Fe_5Cy_{12},12H_2O$—but in neither case were the results more than approximate.

In estimating the iron, the fixed residue, after ignition, was dissolved in strong hydrochloric acid (with a little nitric acid), and precipitated by ammonia. The fixed residue in similar analyses has often been erroneously regarded as ferric oxide, but I found that in one case 0·3162 gram fixed residue yielded 0·3268 gram ferric oxide. It will, therefore, be readily seen that results obtained by regarding the fixed residue as ferric oxide would be valueless when considering two substances so nearly alike in composition as these two blues.

LXIV.—*On the Formation of Hyponitrites.*

By Wyndham R. Dunstan, Professor of Chemistry to the Pharmaceutical Society, and T. S. Dymond.

During the course of some experiments with nitrous oxide, we had occasion to examine the behaviour of ferrous hydroxide towards nitric oxide, nitrites, and nitrates. Since our results differ materially from those obtained by other observers, and are also of some theoretical interest, we think it worth while to lay them before the Society in a separate form.

Zorn (*Ber.*, 15, 1258) has examined the action of ferrous hydroxide on sodium nitrite and nitrate; he states that from both these salts hyponitrite is formed together with ammonia, nitrogen, and nitrous oxide. He prepares the ferrous hydroxide by precipitating ferrous sulphate with milk of lime, so that the mixture is neutral or slightly acid; excess of lime is to be avoided. The nitrite or nitrate is then added to the semi-solid mass of ferrous hydroxide and calcium sulphate. Only one quantitative result is recorded in the paper; from this, it appears that the ferrous hydroxide from 1 kilo. of ferrous sulphate produces from 100 grams of sodium nitrite the equivalent of 10 grams of silver hyponitrite.

Divers and Haga (Trans., 1884, 87) repeated Zorn's experiments with negative results, so far as the formation of hyponitrite is concerned. Later (Trans., 1885, 364) they record the results of further experiments made with ferrous hydroxide suspended in strong potash solution. Under these conditions, it is said that nitrites yield much ammonia, but neither hyponitrite, hydroxylamine, nor any gaseous products. Nitrates are unaffected: experiments were also made with nitric oxide, which is said to be largely converted into ammonia, but to yield no hyponitrite.

Preparation of the Reagents.

The ferrous hydroxide used in our preliminary experiments was prepared by precipitating a solution of ferrous sulphate with a slight excess of potash solution. The light-green precipitate was washed with water until it was free from alkali. Prepared in this way, ferrous hydroxide is a pale-green gelatinous substance, which rapidly oxidises in the air, and when kept for long in contact with water it undergoes what appears to be a physical modification. On this account, when quantitative experiments were made, and it was necessary to have the ferrous hydroxide always in the same condition, and possessed of its full activity, the precipitation was effected, without access of air, with exactly the proper quantity of potash solution, and the mixture used at once When ferrous hydroxide is suspended in strong potash solution, its colour at once changes to a slate-grey, and the substance becomes pulverulent and aggregated. In this condition, it is much less active as a deoxidising agent. Ferrous hydroxide, precipitated together with calcium sulphate, from a solution of ferrous sulphate by milk of lime, is particularly active, and the mixture evolves hydrogen if allowed to stand. It is next to impossible, however, to prepare such a mixture without its being slightly alkaline, that is if the precipitation of the hydroxide is complete, chiefly due to the fact that the lime is only slowly and sparingly soluble. Although Zorn's directions in this respect cannot be practicably carried out, yet we have never found that the small excess of lime interferes at all with the activity of the ferrous hydroxide, while the presence of undecomposed ferrous sulphate, in the reaction with nitrites, may give rise to the formation of nitric oxide. We have never noticed the evolution of hydrogen except under the above-mentioned conditions. A similar mixture prepared with potash instead of lime does not give off any hydrogen, even after prolonged standing. Ammonia cannot be used for the preparation of the ferrous hydroxide, since not only does some of the iron remain in solution, but the hydroxide also retains some ammonia even after much washing, and this is evolved when the hydroxide is digested with a fixed alkali.

The sodium nitrite used in our experiments was derived from silver nitrite prepared according to Victor Meyer's directions (*Annalen*, **171**, 237). Its purity was ascertained by weighing the silver left after ignition, and also by decomposition with excess of aqueous sodium chloride, and titration of the resulting sodium nitrite, in dilute acidified solution, with permanganate. When the sodium nitrite was required for an experiment, it was made by triturating silver nitrite with an equivalent quantity of sodium chloride dissolved in water. The mixture was then rapidly filtered into the vessel in which the reaction was to be effected.

The sodium hydroxide we used was generally freshly prepared from the metal. The potash and soda of commerce were quite useless, since, as one of us has already pointed out (*Pharm. Journ.* [3], **16**, 778), they invariably contain both nitrite and nitrate. The specimens prepared "by alcohol" usually contain nitrate. Starting with the soda of commerce we tried to purify it by heating it with iron, copper, and ammonium sulphate, but these methods for one reason or another, failed to yield the soda in anything like a pure state. Latterly we found that it could be effectively purified by acting for some time on a hot strong solution with sodium amalgam rich in sodium. By this means the nitrite and nitrate are converted into hyponitrite and hydroxylamine, both of which can be decomposed and removed by boiling the liquid.

The nitric oxide was prepared by Pelouze's method from ferrous sulphate, potassium nitrate, and dilute sulphuric acid. It was twice washed with water, and twice with potash solution. Its purity was ascertained by absorption with solution of ferrous sulphate

Reaction of Nitric Oxide with Ferrous Hydroxide and Water.

The ferrous hydroxide prepared by precipitating ferrous sulphate with lime was contained in three flasks which were traversed by the nitric oxide after the air had been expelled from the apparatus by a current of hydrogen. The passage of the nitric oxide was continued for several hours. The filtered liquid contained traces of hyponitrite and some ammonia. The greater part of the nitric oxide had, however, escaped unchanged, and there was some difficulty in ensuring the complete exclusion of air; we therefore resorted to the use of a gas-burette. The most convenient kind for our purpose was a modification of that originally devised by Bunte. It was filled with mercury, and the gas-generating apparatus having been connected with the tap-tube, nitric oxide was drawn into the burette. A mixture of washed ferrous hydroxide and dilute potash solution was then passed into the apparatus through the funnel. In this way the possibility of contamination with air was entirely avoided, and the gas could remain with the hydroxide for any length of time. The mixture was shaken, and during half an hour the gas contracted considerably. The residual gas (nitrogen and nitrous oxide) was then forced out through the tap-tube, and a second instalment of nitric oxide drawn in and allowed to react with the same ferrous hydroxide. When contraction had ceased, this gas was expelled, and a fresh quantity introduced. This process was repeated until the ferrous hydroxide appeared to be completely oxidised, and the nitric oxide was no longer acted on. In all, about 450 c.c. (at 15°) of nitric oxide were used; the residual gas consisted of nitrogen with a little nitrous oxide. The liquid filtered from ferric hydroxide contained hyponitrite and a little ammonia, but no hydroxylamine. Many other similar experiments were made, and the amount of sodium hyponitrite obtained corresponded to from one-fifth to one-tenth of the total weight of nitric oxide used; the best results were obtained when sufficient alkali was added to leave the liquid decidedly alkaline at the close of the experiment. The residual gas always consisted of nitrogen and nitrous oxide, generally with a large preponderance of the former.

When ferrous hydroxide, altered by digestion with strong potash, was used, the nitric oxide yielded much ammonia, nitrogen, and nitrous oxide, but we could detect no hyponitrite. It should be remarked, however, that the detection of very small quantities of hyponitrite in the presence of a large excess of free alkali is a matter of much difficulty, and traces might easily have escaped notice.

Washed ferrous hydroxide in the absence of alkali produces nitrogen and nitrous oxide, but no hyponitrite, ammonia, or hydroxylamine. We have also made experiments with ferrous hydroxide precipitated from ferrous sulphate solution with a moderate excess of potash. In one such experiment, 200 c.c. (at 15°) of nitric oxide were employed, and after agitation for some hours with a mixture of 5 grams of ferrous sulphate and a decided excess of potash solution, 45 c.c. of a mixture of nitrogen and nitrous oxide remained. The liquid contained 0·106 gram of sodium hyponitrite and some ammonia. Thus the nitric oxide originally taken was disposed of in the following manner:—

As nitrogen and nitrous oxide, 85·2 c.c. at 0°.
As sodium hyponitrite, 42·6 c.c. at 0°.
As ammonia (by difference), 61·7 c.c. at 0°.

That is, a little more than one-fifth (0·057 gram) of the total weight of nitric oxide (0·255 gram) became sodium hyponitrite, a little less than one-third became ammonia, and the remainder nitrogen and nitrous oxide. In these experiments, the sodium hyponitrite was precipitated as silver hyponitrite, purified by solution in dilute nitric acid, and reprecipitated by dilute sodium carbonate, then dried, ignited, and the metallic silver weighed. With care, a very fair degree of accuracy may be attained by this process, which is substantially the same as that employed by Divers in his investigation of the composition of silver hyponitrite.

We had noticed when nitric oxide was agitated with ferrous hydroxide, in presence of alkali, that some of the gas is absorbed, and that the mixture after a short time begins to effervesce, and continues to evolve nitrogen for several hours. Experiments were next made to ascertain—

(i.) The influence of alkali on the reaction; and

(ii.) The origin of the nitrogen which is eventually evolved from the liquid.

Nitric oxide and sodium hydroxide were made to react with ferrous hydroxide [$NO : NaOH : 3Fe(OH)_2$]. The nitric oxide (actually 74·6 c.c. at 0°) was contained in the gas burette, the mixture of ferrous sulphate and sodium hydroxide added, and the whole shaken until contraction had ceased; this generally occupied half-an-hour. The liquid was quickly filtered, and the hyponitrite determined by precipitation as silver salt. This experiment was repeated with quantities of sodium hydroxide relatively twice and thrice as great as before, the molecular proportion of the other reagents remaining the same. The series of experiments were then repeated in precisely the same way, only that the mixture remained in the burette until all gas had been evolved; this generally occupied four hours. The amount of hyponitrite was then determined. The results are recorded in Table I:—

TABLE I.

$Fe(OH)_2$, gram.	NO, gram.	NaOH, gram.	$Na_2N_2O_2$, after absorption.	$Na_2N_2O_2$, after effervescence.
0·9	0·1	0·24	0·012	none
0·9	0·1	0·48	0·038	0·017
0·9	0·1	0·72	0·055	0·040

These experiments serve to exhibit the influence of alkali in promoting the formation of hyponitrite, and also the subsequent decomposition of the hyponitrite, by ferrous hydroxide, with evolution of nitrogen. The effect of the alkali appears to reach its maximum in the last experiment, for when larger quantities were added, the yield of hyponitrite was not increased. If on further consideration it should appear desirable to study more fully the conditions of chemical change, we intend to repeat these experiments with much larger quantities of nitric oxide, employing an apparatus we have devised for the purpose. The gas apparatus we used in the above-recorded experiments did not enable us to obtain accurate results when more than 80 c.c. of gas were used.

Reaction of Sodium Nitrite with Ferrous Hydroxide and Water.

About 2 grams of sodium nitrite dissolved in water were mixed, in the gas burette, with washed ferrous hydroxide from 10 grams of ferrous sulphate. In a few minutes, an energetic reaction occurred and gas was copiously evolved, while the ferrous hydroxide rapidly became changed to ferric hydroxide. After the brisk effervescence had ceased, gas was slowly given off for many hours. When action seemed to be over, the gas was removed and found to be almost entirely nitrogen with a very small quantity of nitrous oxide. The liquid contained sodium hydroxide, and with silver nitrite yielded an abundant yellow precipitate of silver hyponitrite; subsequently when more silver nitrite was added a brown precipitate of silver oxide was produced. Not a trace of hydroxylamine was present. We have made many other experiments, and have always observed the formation of an appreciable quantity of hyponitrite. Ferrous hydroxide prepared from lime and ferrous sulphate gave precisely similar results. Ferrous hydroxide and strong potash solution acted much more slowly, but we always obtained some gas, and more or less hyponitrite.

Further experiments were now instituted in order to gain some knowledge of the nature of the reaction. 0·48 gram of sodium nitrite was added to washed ferrous hydroxide from about 12 grams of ferrous sulphate. After 12 hours, 33 c.c. of gas (at 16°) had collected, and the ferrous hydroxide had been completely changed to ferric hydroxide. The composition of the gas was determined by mixing it with hydrogen, and propagating an explosion by means of electrolytic gas (hydrogen and oxygen). It contained—

N	89·4 per cent.
N_2O	10·6 „

The liquid contained besides ammonia 0·013 gram of sodium hyponitrite. In other experiments, we found the volume and composition of the disengaged gas to be largely dependent on the amount of ferrous hydroxide present, as well as on the time during which the action is allowed to continue. Excess of active hydroxide yielded, after some hours, a large quantity of gas, which consisted either entirely or almost entirely of nitrogen, but not a trace of hyponitrite could be detected, although if the action had been stopped an hour after its commencement the liquid would have been found to contain an appreciable quantity. In some instances, when the nitrite was in excess, the gas contained as much as 53 per cent. of nitrous oxide, in others 10 per cent. and less. Once we obtained what was undoubtedly pure nitrous oxide, but we have never again been able to get this result, although we have tried repeatedly under many different conditions. The liquid which remains is always alkaline, partly from ammonia and partly from sodium hydroxide, which is set free during the reaction.

The following experiments were made to ascertain the influence of different quantities of ferrous hydroxide on the formation of the gas, ammonia, and hyponitrite. The ferrous sulphate was first introduced into the apparatus, and exactly sufficient of a solution of sodium hydroxide to precipitate the iron was mixed with the sodium nitrite, and the whole added to the ferrous sulphate. Care was taken that in all cases the same quantity of water was present. The mixture was then allowed to remain until action was completely over, and to ensure this 18 hours were necessary. The temperature was uniformly 16°. The volume of the gas was read off, and its composition ascertained; it consisted of nitrogen, mixed, in one or two instances, with a very small proportion of nitrous oxide. The liquid was divided into two parts. In one of these, the hyponitrite was precipitated as silver hyponitrite with the usual precautions. In the other, the ammonia was determined by distillation in a slow current of air, the distillate being received in standard sulphuric acid. The results are recorded in Table II. A further series of experiments was instituted, where

TABLE II.

$FeSO_47H_2O$, grams.	$NaNO_2$, grams.	Gas evolved. Cubic centimetres at 0°.	NH_3, grams.	$Na_2N_2O_2$ grams.
5	0·748	31·82	0·017	0·104
8	0·748	67·58	0·027	traces
12	0·748	85·66	0·040	none
16	0·748	90·30	0·046	none

the conditions, with one exception, were the same as those in the preceding series. The soda was now added to the ferrous sulphate, and after shaking until the whole of the ferrous sulphate had become hydroxide, the sodium nitrite was introduced. In this way, we were sure that no ferrous sulphate took part in the reaction, either with the nitrite or hyponitrite. Ferrous sulphate rapidly decomposes both these salts. It will be seen that in these experiments, recorded in Table III, although the general course of the reaction is the same as that in the former series, the hyponitrite is not so easily decomposed, and a better yield is obtained. In the first experiment (Table III) sodium nitrite and ferrous hydroxide react in the proportion

$$NaNO_2 : Fe(OH)_2$$

(actually the hundredth of the molecular weight in grams), whilst in the succeeding experiments two, three, and four times as much ferrous hydroxide was employed, the quantities of the other compounds present, including the water, remaining constant. It appears then from these experiments, as well as from our former observations, that the sodium nitrite is first converted into ammonia, nitrogen, and hyponitrite, or at least into some compound which forms silver hyponitrite from silver nitrate, and this hyponitrite (actual or potential) is then decomposed by ferrous hydroxide with production of more nitrogen. When excess of ferrous hydroxide is present, the whole of the sodium nitrite is eventually entirely converted into ammonia and nitrogen, as is seen from the last experiment recorded in Table II. If the temperature is allowed to rise, the amount of the gas obtained is increased, while the quantity of hyponitrite is diminished.

TABLE III.

$FeSO_4 7H_2O$, grams.	$NaNO_2$. grams.	Gas evolved. Cubic centimetres at 0°.	NH_3, grams.	$Na_2N_2O_2$, grams.
2·78	0·69	16 76	0·013	0·096
5 56	0·69	46 60	0·019	0·113
8·34	0·69	68·70	0·020	0·011
11·12	0·69	87·70	0·027	trace

As a lecture experiment to illustrate the formation of sodium hyponitrite from ferrous hydroxide and sodium nitrite, we recommend the following method:—5 grams of ferrous sulphate are dissolved in about 25 c.c. of water, and enough of a 10 per cent. solution of potash is added to leave the mixture decidedly but not strongly alkaline. A solution of about 1 gram of sodium nitrite in 25 c.c. of water is then added, and the whole well stirred. After a few minutes, effervescence will begin and continue for some time. At the end of half an hour the mixture, which smells strongly of ammonia, is filtered, diluted with an equal volume of water, and precipitated with a few drops of silver nitrate solution. The pale-yellow precipitate of silver hyponitrite will be very distinct, unless indeed much alkali is present, when the liquid will need to be neutralised with dilute acetic acid. We have frequently noticed that the mixture on standing darkens from reduction of silver, and at first we attributed this to hydroxylamine. We have since proved that hydroxylamine is not present, and that the effect is probably due to a trace of unconverted ferrous salt. It disappears if the liquid is allowed to stand for some time. The solution has a brownish colour, and evidently contains a little iron in the ferric condition, and soon deposits a small quantity of ferric hydroxide. Whether this iron is in a state of suspension or solution is difficult to determine on account of its very small quantity, but from other experiments we believe it to be unconnected with the formation of the hyponitrite. Sodium nitrite when acted on as above described yields about 6 per cent. of sodium hyponitrite.

In order to throw further light on the exact origin of the nitrogen, nitrous oxide, and ammonia, we made experiments with ferrous hydroxide in reaction with sodium hyponitrite and with hydroxylamine.

Reaction of Ferrous Hydroxide with Sodium Hyponitrite and Water.

The funnel of the gas-burette was plugged to act as a filter, and in it was placed about 1 gram of pure moist silver hyponitrite prepared from the reaction of sodium amalgam and sodium nitrite, and many times purified from possible traces of silver nitrite. A solution of sodium chloride was immediately added, and the sodium hyponitrite that was instantly formed was drawn into the body of the burette, which already contained ferrous hydroxide. After 12 hours a little nitrogen had been evolved, and it was evident that the salt was being slowly decomposed. When nearly all action had ceased, the liquid was filtered and examined for hydroxylamine and ammonia. Not a trace of either was present; the liquid was not even coloured by Nessler's solution.

Reaction of Sodium Hyponitrite with Sodium Amalgam and Water.

The foregoing experiment was repeated with a mixture of sodium amalgam and water. The sodium hyponitrite was slowly decomposed, but not a trace of hydroxylamine or ammonia was formed. It is to be remembered that both ammonia and hydroxylamine are formed when sodium amalgam reacts with water and sodium nitrite.

Reaction of Hydroxylamine with Ferrous Hydroxide and Water.

A solution of hydroxylamine hydrochloride was made faintly alkaline with sodium hydroxide, and added to some washed ferrous hydroxide contained in the gas-burette. The hydroxylamine was instantly decomposed, much ammonia was formed, and a little nitrogen.

Reaction of Sodium Nitrate with Ferrous Hydroxide and Water.

We have made a large number of experiments with alkali nitrates, but have never succeeded in obtaining anything but doubtful traces of hyponitrite. When active ferrous hydroxide is used, a very slight action occurs after many hours, a few bubbles of gas (nitrogen ?) are formed, some ammonia is produced, but no hydroxylamine. We also found, when silver nitrate solution was added to the filtered liquid, that a slight yellow opalescence appeared, possibly due to a trace of hyponitrite, but the quantity was so minute, if indeed there was any, that we are unable to speak more definitely. Quantitative experiments showed that small quantities of potassium nitrate are entirely converted into ammonia by contact with active ferrous hydroxide. 0·052 gram of potassium nitrate was allowed to remain in contact with ferrous hydroxide, prepared by precipitating 5 grams of ferrous sulphate with a slight excess of sodium hydroxide. After eight hours, no gas had been evolved, and the liquid contained 0·0098 gram of ammonia, a practical coincidence with the calculated amount, 0·01 gram. One gram of potassium nitrate with the hydroxide from 5 grams of ferrous sulphate yielded, after 48 hours, only 0·0208 gram of ammonia, and the majority of the ferrous hydroxide was unacted on. Ferrous hydroxide changed by contact with strong potash solution is without action on alkali nitrates.

We attempted to compare the reaction of alkali nitrates and silver nitrate with ferrous hydroxide, in the hope of being able to throw some light on the constitution of nitrates. Russell's experiments with respect to the action of hydrogen on silver nitrate appear, as has been pointed out by Divers, to lend support to that view of the constitution of nitrates which is expressed by the general formula $M'ONO_2$, and it seemed probable that one atom of oxygen (that supposed to be in union with the metal) might be more readily detached from silver nitrate by ferrous hydroxide than from potassium or sodium nitrate. The experiment failed in its object for an unexpected reason. When washed ferrous hydroxide is mixed with a solution of silver nitrate, double decomposition occurs at once. Ferrous nitrate remains dissolved, and the silver oxide at first formed rapidly becomes metallic silver by contact with excess of ferrous hydroxide. Ferrous nitrate, like sodium nitrate, is only very slowly acted on by excess of ferrous hydroxide.

Discussion of Results.

So far as the action of ferrous hydroxide on nitrites is concerned our results confirm the original statement of Zorn that hyponitrite is formed, but we find, contrary to his experience, that nitrates are hardly affected at all. We are unable to confirm the statement made by Divers and Haga that ferrous hydroxide in presence of alkali does not form hyponitrite from nitric oxide.

We now proceed to a discussion of the results we have obtained.

With nitric oxide in the presence of alkali, there are apparently two distinct reactions to be considered. The one consists in the direct reduction of the nitric oxide to nitrogen; in the other, with which we are particularly concerned, nitric oxide is absorbed with formation of ammonia and hyponitrite, then this salt disappears with evolution of nitrogen. The formation of the hyponitrite may be generally expressed by the equation $2NaOH + 2NO + 2Fe(OH)_2 = Fe_2(OH)_6 + Na_2N_2O_2$. The hyponitrite next yields nitrogen. $Na_2N_2O_2 + 2Fe(OH)_2 + 2H_2O = Fe_2(OH)_6 + 2NaOH + N_2$. The formation of ammonia, only in presence of alkali, will be more conveniently discussed later.

In the absence of alkali, nitric oxide is reduced to nitrous oxide and nitrogen.

The reaction of ferrous hydroxide with sodium nitrite may be represented by the two equations

$$2NaNO_2 + 2H_2O + 4Fe(OH)_2 = Na_2N_2O_2 + 2Fe_2(OH)_6;$$
$$Na_2N_2O_2 + 2Fe(OH)_2 + 2H_2O = Fe_2(OH)_6 + 2NaOH + N_2$$

These two reactions appear to proceed simultaneously. We have shown that ferrous hydroxide does not produce either hydroxylamine or ammonia from hyponitrite. In order, therefore, to understand how the ammonia originates, the constant formation of which is an important feature of the reaction, we must assume the existence of some intermediate or transition compound. It will be simpler to discuss first, the formation of hyponitrite from sodium amalgam and a solution of sodium nitrite, a reaction which led to the discovery of these salts by Divers in 1871. There are two features of this reaction which are of especial importance in the present connection: the first is the constant production of hydroxylamine as well as hyponitrite; the second is the fact, established by us in the present communication, that neither the hydroxylamine nor ammonia are derived from a further action of sodium amalgam on the hyponitrite. Dr. Divers in his original communication, printed in the *Proceedings of the Royal Society* for 1871, and also in subsequent communications to this Society, more particularly in that important one entitled "The Production of Hydroxylamine from Nitric Acid," regards the formation of hyponitrite as due to the direct *withdrawal* of oxygen from the nitrite or nitrate by the metal $2NaNO_2 + 2Na_2 = Na_2N_2O_2 + 2Na_2O$, but this suggested mode of action furnishes no account of the formation of hydroxylamine. In a later paper, Dr. Divers makes the suggestion, in another connection, that a compound of the formula $NaNONa_2$ is formed by the *substitution* of two atoms of sodium for one of oxygen in the nitrite, $NaNO_2 + 2Na_2 = NaNONa_2 + Na_2O$, and that this is subsequently decomposed by water, yielding hydroxylamine and sodium hydroxide, $NaNONa_2 + 3H_2O = 3NaOH + NH_2OH$ (see Divers, Trans., 1883, 458). Neither of these suggestions is sufficient to account for the simultaneous production of hydroxylamine and hyponitrite.

The hypothesis we wish to suggest as at once the simplest and most in accordance with the facts, supposes that the sodium nitrite first directly combines with two atoms of hydrogen. The formula of the new compound will be $Na\cdot N:(OH)_2$, or perhaps $NaONH\cdot OH$. This substance will on the one hand split up into sodium hyponitrite and water, $2NaN(OH)_2 = Na_2N_2O_2 + 2H_2O$, and on the other be acted on by hydrogen, yielding hydroxylamine and sodium hydroxide, $NaN(OH)_2 + H_2 = NH_2\cdot OH + NaOH$. More hydrogen will yield ammonia, and the hydroxylamine itself will be largely converted into ammonia and nitrogen by the alkali $3NH_2\cdot OH = N_2 + NH_3 + 3H_2O$. It is not necessary for the purposes of this hypothesis that hydrogen should be set free, even momentarily. It concerns the simultaneous action of two compounds, sodium nitrite and sodium, on a third, water, the hydroxyl of which is seized by the sodium and the hydrogen by the nitrite.

$$\begin{matrix}Na\\Na\end{matrix} + \begin{matrix}OH\cdot H\\OH\cdot H\end{matrix} + \begin{matrix}O\\O\end{matrix}NNa = \begin{matrix}Na\cdot OH\\Na\cdot OH\end{matrix} + \begin{matrix}HO\\HO\end{matrix}NNa.$$

If crystalline sodium amalgam, which is relatively poor in sodium, is mixed with cold water, little or no action occurs until sodium nitrite is added, when a vigorous effervescence ensues; the escaping gas contains no hydrogen, but consists wholly of nitrogen and nitrous oxide.*

We believe that this hypothesis will serve also to explain the results we have obtained with ferrous hydroxide. This substance, as is well known, readily passes into ferric hydroxide, and we have noticed that under some conditions it is able by itself to decompose water, combining with the hydroxyl and liberating the hydrogen. So that it may, like sodium amalgam, be regarded as a compound that is ready to combine with hydroxyl, and which will decompose water provided that some substance is also present to combine with the hydrogen. Such a substance is, *ex hypothesi*, sodium nitrite, and the interaction of these three compounds may be represented thus:—

---

* Professor Armstrong has pointed out to one of us that the conditions which obtain here may be regarded as those of a voltaic cell in which the amalgam forms one plate and the nitrite the other.

$$\begin{matrix}Fe(OH)_2\\Fe(OH)_2\end{matrix} + \begin{matrix}OH{\cdot}H\\OH{\cdot}H\end{matrix} + \begin{matrix}O\\O\end{matrix}NNa = \begin{matrix}Fe(OH)_3\\Fe(OH)_3\end{matrix} + \begin{matrix}HO\\HO\end{matrix}NNa.$$

The $NaN(OH)_2$ will then decompose into hyponitrite and water, and in reaction with more ferrous hydroxide will yield nitrogen and ammonia, $8NaN(OH)_2 + 6H_2O + 14Fe(OH)_2 = 8NaOH + 7Fe_2(OH)_6 + 3N_2 + 2NH_3$. If excess of ferrous hydroxide acts for a long time, the whole of the nitrite will be decomposed in accordance with the second equation. If it is necessary, we may also assume that some hydroxylamine is momentarily formed: $2Fe(OH)_2 + NaN(OH)_2 + 2H_2O = Fe_2(OH)_6 + NaOH + NH_2OH$, and at once decomposed by ferrous hydroxide. The hyponitrite formed will also be subsequently decomposed if excess of ferrous hydroxide is present, yielding nitrogen and sodium hydroxide. The nitrous oxide which is sometimes formed is no doubt a result of the hydrolysis of sodium hyponitrite, $Na_2N_2O_2 + H_2O = 2NaOH + N_2O$.

The formation of hyponitrite from nitric oxide is more difficult to explain. The products of its reaction with ferrous hydroxide in presence of alkali are the same as those of sodium nitrite, namely, hyponitrite, ammonia and nitrogen. We could get no evidence of the existence of an intermediate nitro-ferrous compound similar to the nitro-stannous compound which Divers believes to be formed when stannous oxide in presence of alkali produces hyponitrite from nitric oxide. When ferrous hydroxide reacts in the absence of alkali, the nitric oxide is rapidly reduced to nitrous oxide and nitrogen, but no hyponitrite or ammonia is formed. The presence of alkali is the determining cause of the formation of hyponitrite and ammonia, and although the production of hyponitrite might be explained by the union of "nascent" nitrous oxide or its isomeride with the alkali, we think the absorption of nitric oxide by the mixture and the simultaneous formation of ammonia and hyponitrite point to the intermediate existence of the same compound, $NaN(OH)_2$, that we have suggested is formed under similar conditions from a nitrite.

Alkali nitrates, which in aqueous solution readily react with sodium amalgam, forming hyponitrite and hydroxylamine, are only very slowly attacked by ferrous hydroxide. This difference appears to be consistent with the known fact that the former substance is the more powerful deoxidising agent.

LXV.—*The Reaction between Sulphites and Nitrites of Metals other than Potassium.*

By Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S., Imperial University, Tôkyô, Japan.

Our production of hydroxylamine from nitrites by means of hydrogen sulphide, already recorded (this vol., p. 48), led us to experiment with nitrites and sulphites. It was already known, from Claus's work on Fremy's series of potassium salts, that when potassium sulphite in solution is added to potassium nitrite, a salt, $HON(SO_3K)_2$, is one of the products, and that this salt if heated in solution yields $HONH(SO_3K)$, together with potassium hydrogen sulphate. Claus proved the latter salt to be potassium hydroxylamine-monosulphonate, and, since the appearance of his papers, the former salt has been recognised, in the light of V. Meyer's researches on the oximido-radicle, to be potassium hydroxylamine-disulphonate.* But as the formation of such salts is peculiar to potassium compounds, there remained to be determined what might be the action of sulphites upon nitrites when the base was not potassium.

First, we found that silver nitrite and mercurous nitrite† were both decomposed by sulphurous acid added in moderate excess, yielding at once an insoluble sulphite of the metal, and some nitric oxide and sulphuric acid; and after boiling away the excess of sulphurous acid the solution gave, as evidence of the presence of hydroxylamine, a good precipitate of cuprous oxide with alkali and copper sulphate. When, instead of at once boiling off the unused sulphurous acid, the solution was allowed to stand several hours before this was effected, the hydroxylamine reaction could no longer be obtained. (In presence of sulphurous acid, the copper test for hydroxylamine is inapplicable.) We then tried the action of sulphurous acid upon hydroxyammonium chloride, and found that the hydroxylamine slowly disappeared from the solution. In a paper, which has quite recently appeared (*Ber*, 20, 584), Raschig states that when hydroxylamine and sulphurous acid are brought together, amine-sulphonic acid, $H_2N{\cdot}SO_3H$, is formed; this explains the disappearance of the hydroxylamine which we observed.

---

* Raschig (*Ber.*, 20, 584) states that Claus attributed to the disulphonic salt the constitution $O : NH(SO_3K)_2$, but in this he is not quite accurate, since Claus expressly mentions (*Annalen*, 158, 83) that he has made no decision between that formula and $(HO)N(SO_3K)_2$.

† Concerning the preparation and properties of this new salt, we have yet to publish an account.

It is somewhat remarkable, however, that sulphurous acid can be boiled away from as yet unchanged hydroxyammonium chloride without destroying it.

We next treated a solution of sodium nitrite with sulphurous acid solution, and obtained here, too, some nitric oxide and sulphuric acid, and, after boiling off excess of sulphurous acid, found much hydroxylamine present. In this case, it was easy to go farther in the examination of the reaction than when the nitrites used were insoluble, and we modified our experiments by adding the sodium nitrite to the sulphurous acid until the latter was just destroyed, thus enabling us to test in the cold for hydroxylamine. The result was negative; on the contrary, after boiling the solution and again testing, abundance of hydroxylamine was found. It thus became certain that an intermediate compound was formed in the reaction.

Sodium sulphite and metasulphite were then used in place of the sulphurous acid.

If sodium sulphite and sodium nitrite in solution are mixed, then acidified and boiled, hydroxylamine is formed, and, when the sulphite is in the proportion of 2 mols. to 1 of the nitrite, and the hydrochloric acid is added very slowly, almost all the nitrogen is found, on titration with iodine, to have been converted into hydroxylamine,

$$NaNO_2 + 2Na_2SO_3 + OH_2 + 4HCl = HONH_3,HCl + 3NaCl + 2NaHSO_4.$$

On evaporating the acid solution, separating the sodium salts by alcohol, and evaporating again, hydroxyammonium sulphate crystallises out. If the solution containing the mixed sulphite and nitrite is suddenly acidified, sulphur dioxide and nitrous oxide escape with effervescence, and if other proportions of the salts are taken, the hydrochloric acid sets free either sulphurous acid or nitrous acid (nitric and nitrous oxides). In these circumstances, much less hydroxylamine is found.

When sodium metasulphite, $Na_2S_2O_5$, is added to sodium nitrite, a marked rise in temperature is observed, but no escape of gas. The mixture becomes strongly alkaline, and does not show the presence of any hydroxylamine, even after boiling, until it has been first acidified and then boiled. The metasulphite appears to be the best salt to use in making hydroxylamine from nitrite.

Raschig points out (*op. cit.*) what escaped the notice of Claus, that potassium hydroxylamine-sulphonate, heated with water, is changed into the acid sulphates of potassium and hydroxyammonium, and that the sulphonate may therefore be used as a cheap source of hydroxylamine. We believe that the use of sodium salts in place of potassium salts will materially facilitate this method of preparing hydroxylamine.

The production of hydroxylamine from silver, mercury, and sodium nitrites in the way above described has been known to us for more than a year, but we have been unwilling to publish it until we should be able to describe the stages of the reaction between the two sodium salts. We are led to send this communication at once* to the Society, for fear lest we should be anticipated by Raschig in the publication of a fact of considerable interest, which we have observed and are now investigating, and which we here proceed to describe to the extent to which we have as yet examined it.

It is current in chemical literature that Fremy could not obtain any sodium compound corresponding with his potassium salts.† We find, however, that both hydroxylamine-sulphonates and amine sulphonates of sodium are producible directly from the sulphite and nitrite. It is true that when solutions, even somewhat concentrated, of sodium sulphite and nitrite are mixed, no separation of crystals occurs as when potassium salts are used, and that the sulphite can be, for the most part, again separated from the nitrite by precipitating it as barium salt. But this must be done quickly. Soon after the solutions are mixed, a slight rise in temperature is generally noticeable, and the mixed solutions exhibit the property, which neither sulphite nor nitrite apart possesses, of absorbing much carbon dioxide. We have already mentioned that metasulphite and nitrite, which apart are neutral in reaction, yield a very alkaline mixture. The power of absorbing carbon dioxide is gradually developed, at first somewhat rapidly, then more and more slowly. Thus, 8·5 c.c. of normal solution of the sulphite mixed with 4·25 c.c. of normal solution of nitrite (2 mols., therefore, to 1), both solutions before mixing having been saturated with carbon dioxide, were enclosed in a graduated vessel over mercury, along with carbon dioxide. In the first two days, about 200 c.c. of gas had been absorbed, during the next eight days an additional 75 c.c., and after that no more. The temperature of the air varied greatly, but as a mean was about 14°. The gas and solution were frequently shaken together, and it was thus noticed that the solution which could soon be temporarily saturated with the gas by agitation with it, gradually regained, on standing at rest, the power to absorb a fresh quantity when again shaken. In this way it was possible to observe the progress of the reaction between the nitrite and sulphite. With barium chloride, the resulting solution gave a precipitate of carbonate and another salt. The precipitate dissolved almost perfectly in hydrochloric acid, without giving any odour of sulphur dioxide, and the solution on heating deposited barium sulphate, and then gave evidence of containing much hydroxylamine, although before heating no hydroxylamine could be detected. The filtrate from the original barium precipitate contained a very little unchanged nitrite, and also gave, when acidified and boiled, much barium sulphate, but only a very slight reaction with copper for hydroxylamine. Free ammonia was absent, but cupric hydroxide dissolved with a blue colour. The original solution (unmixed, that is, with barium chloride), when left freely exposed to the air, did not oxidise to sulphate, as sulphite would, and on evaporation gave crystals of a salt which by its reactions appeared to be undoubtedly sodium hydroxylamine-disulphonate.

---

* By first mail after the arrival here of the number of the *Berichte* containing Raschig's paper, and which leaves Tôkyô on May 4th.

† Unable here to consult Fremy's paper, published in 1845, on the compounds which potassium nitrite forms with potassium hydroxide and sulphur dioxide, we make this extract from *Miller's Chemistry* (1864), ii, 196, and later editions:—"It is remarkable that if nitrite of sodium be substituted for nitrite of potassium, no sulphazotised salts are formed. Indeed, Fremy was unable to procure any such compound which contained sodium."

We have as yet gone no farther, but the results obtained make us certain that hydroxylamine-disulphonate and amine-trisulphonate are formed by the action of sodium sulphite upon nitrite, although more slowly than when potassium salts are used.* The reaction between the sodium salts proceeds for a time without the assistance of carbon dioxide, though certainly more slowly, but it is doubtful whether the change can be completed without it. Further experiments on this point are in progress, and others will be instituted. The proportions of salts and gas consumed in the experiment recorded indicate the occurrence of a reaction expressed by the equation—

$$NaNO_2 + 2SO_3Na_2 + 3CO_2 + 2OH_2 = HON(SO_3Na)_2 + 3CO_3NaH,$$

followed to some extent by that expressed by—

$$HON(SO_3Na)_2 + SO_3Na_2 + CO_2 = N(SO_3Na)_3 + CO_3NaH.$$

Raschig calls attention to the evidence which the production of Fremy's salts affords of sulphites being hemihaloïd salts. One of us in previous papers to the Society, has already maintained the sufficiency of the evidence to be gained from reactions in purely inorganic chemistry as to the constitution of sulphites, and we now submit to the judgment of others the additional and convincing proof afforded by the reactions above formulated, that sulphites are not dioxylic salts, but hold half their metal unoxidised and in direct union with the sulphuryl. For we see in these reactions the nitrite deoxidised, not by the sulphite becoming sulphate, but by half its sodium taking oxygen from the nitrite and appearing as carbonate or hydroxide. Were the sulphite a dioxylic salt, $SO(ONa)_2$, would the sodium leave the oxygen of the sulphite for that of the nitrate?

---

* Even in the case of potassium salts, according to Claus, reaction may continue for more than a week, when the solutions are dilute.

We shall make known to the Society the results of our examination of the new sodium salts as soon as we have obtained them, hoping meanwhile that Dr. Raschig in his promised further researches on the reaction between nitrous and sulphurous acids may leave this part of the subject to be worked out by us.

LXVI.—*Anacardic Acid.*

By Dr. S. Ruhemann and S. Skinner.

The fatty oil contained in the shell of the fruit of *Anacardium occidentale* has already been investigated by Staedeler (*Annalen*, **63**, 137). He found that this oil consists of an acid, anacardic acid, melting at 26°, and a substance "cardol," which has an irritating action similar to that of cantharidine when applied to the skin. As we had the opportunity of obtaining a large quantity of these seeds, we have made the oil, which occurs in great abundance in them, the subject of a closer study. This was moreover desirable as the formula $C_{44}H_{32}O_7$ (*old notation*), which Staedeler derived from his analyses, cannot easily be translated if the new atomic weights are used.

For the extraction of the acid, the shells are treated according to Staedeler's directions. The ethereal extract thus obtained, after the removal of the ether, is saponified with recently precipitated lead hydroxide in dilute alcoholic solution, and then filtered. The residue remaining on the filter containing the lead salt of the acid is suspended in water, decomposed with ammonium sulphide, filtered from lead sulphide, and the acid separated from the ammonium salt by means of dilute sulphuric acid. The anacardic acid rises as an oil to the surface, and solidifies on cooling. After a further purification effected by repeating this process, the acid has the melting point given by Staedeler. On evaporating the alcoholic solution from the lead salt, it gives a thick red oil, the cardol.

Up to the present time we have been occupied with the study of anacardic acid, and now desire to communicate the results already obtained. The investigation of our preparation, and of one from Dr. Schuchart, leads to the conclusion that this compound has the formula $C_{22}H_{32}O_3$, and is to be regarded as a hydroxycarboxylic acid. The analysis of the acid dried at 100° (at which temperature no decomposition takes place) gave the following results:—

	Theory.		Found by R and S.		
			I.	II.	By Staedeler
C_{22}	264	76·7	76·25	76·31	75·06
H_{32}	32	9·3	9·3	9·31	9·17
O_3	48	14·0	—	—	—
	344	100·0			

This formula for the acid is further verified by the analysis of its salts

The *silver salt* is thrown down as a white precipitate on adding silver nitrate to the alcoholic solution of the acid, nitric acid being set free. The analysis of this salt, dried at 100°, showed it to have the following composition, $C_{21}H_{31}O{\cdot}COOAg$, which requires—

	Theory.		Found.			
			I.	II.	III.	IV
C_{22}	264	58·53	58·00	58·73	—	—
H_{31}	31	6·87	7·13	7·31	—	—
Ag	108	23·94	—	—	23·75	23·9
O_3	48	10·66	—	—	—	—
	451	100·00				

The silver salt prepared in this way is comparatively stable, as it can be dried at 100° without discoloration; if, however, silver nitrate is added to an ammoniacal solution of the acid, a white precipitate is formed, which is very unstable, and decomposes after a short time. Apparently this salt contains a second atom of silver, displacing the hydrogen in the hydroxyl group.

The barium, calcium, and magnesium salts are all formed as white precipitates in ammoniacal alcoholic solutions of the acid, but not in solutions of the free acid.

The barium salt gave on ignition with H_2SO_4—

$BaSO_4$.	
I.	II.
46·28	46·39

this corresponds to the formula $C_{21}H_{30}\left\{\begin{matrix}O\\COO\end{matrix}\right\}Ba + H_2O$, which requires 46·8 per cent. $BaSO_4$.

The calcium salt gave numbers which indicate the composition $C_{21}H_{30}\left\{\begin{matrix}O\\COO\end{matrix}\right.Ca + 2H_2O$. This requires 32·53 per cent. $CaSO_4$, whilst we found—

I.	II.
32·76	32·6

The magnesium salt gave on ignition 10·37 per cent. MgO, which corresponds to the formula $C_{21}H_{30}\left\{\begin{matrix}O\\COO\end{matrix}\right\}Mg + H_2O$.

The lead salt was prepared by Staedeler's method, namely, by adding a boiling solution of anacardic acid in alcohol to a boiling solution of lead acetate in alcohol. On standing, a white substance is deposited on the sides of the vessel. This gave on analysis 40·7 per cent. of lead oxide; the formula $C_{21}H_{30}\left\{\begin{matrix}O\\COO\end{matrix}\right.Pb$ requires 40·6 per cent.

The Methyl Salt.—Staedeler states that the acid does not form any ethereal salts when its alcoholic solutions are saturated with hydrogen chloride, we therefore adopted the method of acting on the silver salt with methyl iodide. A few grams of the silver salt were digested with methyl iodide, filtered from silver iodide, and the excess of methyl iodide was removed by distillation from the water-bath. A thick liquid was left, which did not solidify in a freezing mixture. Analysis of a portion of this substance, dried at 100°, showed it to be the methyl salt.

		Theory for $C_{21}H_{30}\left\{\begin{matrix}OH\\COOCH_3\end{matrix}\right.$.	Found.
C_{23}	276	77·09	77·10
H_{34}	34	9·49	9·73
O_3	48	13·42	—
	358	100·00	

This methyl compound is decomposed by distillation, carbon dioxide is evolved, and products of low and high boiling points come over. Similar products are obtained by distilling the acid. On warming this methyl salt on the water-bath with acetyl chloride, hydrogen chloride is given off, and an oil is formed which is methyl acetylanacardate. Its analysis, together with the further study of the acid, we hope shortly to communicate to the Society.

University Laboratory,
Cambridge.

LXVII.—*Sulphinic Compounds of Carbamide and Thiocarbamide.*

By GEORGE MCGOWAN, Univ. Coll. of North Wales, Bangor.

THE results of two previous papers communicated to the Society by the author (Trans., 1886, 191; 1887, 378), on various dihaloid and other derivatives of dithiocarbamide, led naturally to the inquiry whether similar compounds with organic acid radicles could be obtained. That they can be is proved by the preparation of the following compound.

Dithiocarbamide Di-trichloromethyl-sulphinate, $(CSN_2H_4)_2(CCl_3SO_2)_2$.

This, which is analogous to the dichloride $(CSN_2H_4)_2Cl_2$, the dinitrate $(CSN_2H_4)_2(NO_3)_2$, &c., can be prepared quite easily by the action of trichloromethyl-sulphinate of ammonium, $CCl_3{\cdot}SOONH_4$,* on dithiocarbamide dichloride. To a rather concentrated *cold* aqueous solution of the dichloride, a concentrated solution of the sulphinic salt is added. For instance, in one operation, 1·8 gram dichloride, dissolved in about 10 c.c. water and 4 grams sulphinate (containing some ammonium chloride), were used. Masses of very fine needles soon began to separate out.

After standing for some little time, until the quantity of crystals no longer appeared to increase, they were collected and washed with water till free from ammonium chloride (although they were not by any means insoluble in water), then pressed between paper, and finally dried over sulphuric acid in a vacuum.

0·2480 gram gave 22·3 c.c. N at 7° and 779 mm. mercury pressure .... = 11·18 p.c. N.
Calculated for $(CSN_2H_4)_2(CCl_3SO_2)_2$ .... = 10·83 „

The reaction therefore is simply $(CSN_2H_4)_2Cl_2 + 2CCl_3{\cdot}SOONH_4 = (CSN_2H_4)_2(CCl_3SO_2)_2 + 2NH_4Cl$. It is not advisable to use an alcoholic instead of an aqueous solution, because then a much greater volume of solvent is required, and the evaporation which is necessary causes decomposition, with separation of sulphur.

---

* This salt is readily prepared by treating trichloromethyl sulphonic chloride, $CCl_3{\cdot}SO_2Cl$, with strong aqueous ammonia, and evaporating the solution until the salt begins to crystallise out (Loew, *Zeit. Chem.*, 1869, 82). If wanted pure, it can be freed from ammonium chloride by recrystallisation. As it decomposes rather quickly on keeping, it is best to prepare it fresh each time it is wanted. Much heat is absorbed during its solution.

That this is a *di*thiocarbamide compound is certain from the fact that its solution at once yields the characteristic dinitrate,

$$(CSN_2H_4)_2(NO_3)_2,$$

with dilute nitric acid, and immediately gives a precipitate of sulphur on the addition of caustic alkali, or on heating. The addition of hydrochloric acid greatly retards this deposition of sulphur, exactly as in the case of the dichloride, but does not prevent it. Bromine, of course, at once precipitates trichloromethylsulphonic bromide, $CCl_3{\cdot}SO_2Br$. This compound is much more soluble in alcohol than in water, and crystallises from the alcoholic solution on a microscopic slide in stellate groups of the finest needles, in shape not unlike that of a starfish. These are different in appearance from the more rounded groups—likewise of fine needles—of the compound to be mentioned further on, and whose composition is probably expressed by the formula $CSN_2H_3{\cdot}CCl_3SO_2$. It melts at 124—125°.

Thiocarbamide Trichloromethyl-sulphinate, CSN_2H_4,CCl_3SOOH.

This is formed by dissolving thiocarbamide and trichloromethylsulphinate of ammonium in absolute alcohol in molecular proportions, and adding a distinct but not too large excess of concentrated hydrochloric acid; too much alcohol should not be used. Chloride of ammonium separates out, and the alcoholic filtrate on evaporation deposits crystals of the above compound, which may be freed from ammonium chloride by recrystallisation from a *small* quantity of water, and from sulphur by digestion with carbon bisulphide. It is much better to use alcohol than water in the first instance, as the evaporation—especially by heating—of solutions containing sulphinic acid compounds of thiocarbamide, always causes decomposition to a considerable extent, with separation of sulphur.

After being dried over sulphuric acid, the crystals were analysed.

I. 0·3262 gram gave 30·1 c.c. N at 11° and 746 mm. mercury pressure = 10·80 per cent. N.

II. 0·2333 gram, ignited with lime, gave 0·3854 gram AgCl = 40·87 per cent. Cl.

	N.	Cl.
Calculated for $CSN_2H_4,CCl_3{\cdot}SOOH$...	10·79	41·04 p. c.
Found..........................	10 80	40·87 „

The above reaction is therefore expressed by the equation—

$$CCl_3{\cdot}SOONH_4 + CSN_2H_4 + HCl = CSN_2H_4,CCl_3{\cdot}SOONH_4 + NH_4Cl.$$

This compound is readily soluble in water, even more so in absolute alcohol, and also fairly soluble in ether,[*] its solution in any one of these being strongly acid to test-papers. It is not at all deliquescent. If slowly crystallised from water, it separates in beautiful well-developed flat prisms, laid on to each other in layers, and showing colours with polarised light. It melts at 139°, evidently with effervescence and deposition of sulphur. The aqueous solution appears to deposit sulphur slowly on heating. Addition of caustic alkali causes no precipitation of sulphur, at least no immediate precipitation, but an alliaceous odour is evolved. (Difference from *di*thiocarbamide compounds.) Bromine throws down, of course, the sulphonic bromide $CCl_3{\cdot}SO_2Br$.

Carbamide Trichloromethyl-sulphinate, $CON_2H_4,CCl_3.SOOH$.

This, the corresponding compound of carbamide, can be prepared in somewhat the same way as the thiocarbamide compound, only—on account of its instability—the use of water as solvent and of aqueous hydrochloric acid must be avoided. Carbamide and ammonium trichloromethyl-sulphinate (which need not be free from ammonium chloride) are dissolved in a little *absolute* alcohol, in approximately molecular proportions, and hydrochloric acid gas is passed through the solution, too large an excess of gas being avoided. For instance, 2·25 grams carbamide and 9 grams of the somewhat impure sulphinate were dissolved in 30 c.c. alcohol. The precipitated ammonium chloride is filtered off, and the filtrate evaporated to dryness, in the cold, in a vacuum. In this way, a syrupy mass of crystals is ultimately got, which is pressed dry between paper, to free it from hydrochloric and sulphinic acids, and recrystallised, first from absolute alcohol, and finally from absolute ether, carbamide and ammonium chloride being quite insoluble in the latter. (Much heat is absorbed by the solution of this compound, and indeed of trichloromethylsulphinic acid compounds generally.) A portion, thus crystallised from ether, was powdered, pressed between paper, and placed over sulphuric acid in a vacuum for analysis.

0·4021 gram gave 38·45 c.c. N at 12° and
772 mm. mercury pressure .... = 11·53 p. c. N.
Calculated for $CON_2H_4,CCl_3{\cdot}SOOH$ .... = 11·50 „

The above compound is extremely soluble in water and in cold absolute alcohol, and also readily soluble in cold ether, but insoluble in benzene. It cannot be recrystallised from water, as the solution quickly begins to decompose, trichloromethyl-sulphinic acid and sulphur dioxide being set free. It is thus much less stable than the thiocarbamide compound. From ether and from alcohol, it separates in radiating groups of indistinct thin prisms, but I have been unable to get well-formed crystals, owing to the salt remaining in solution until the latter became syrupy, after which crystallisation spread rapidly through the whole mass. The melting point is not sharp. It appears to begin to melt at about 90°, but is not completely melted until the temperature rises to 96—100°; this is no doubt due to the dissociation of the salt and ultimate solution of the carbamide in the acid. Its fresh aqueous solution at once yields carbamide nitrate, CON_2H_4,HNO_3, with nitric acid.

---

[*] From this last, it soon begins to separate in spongy masses of the finest needles, which, however, are not the pure compound, but apparently a mixture of it with thiocarbamide. Thus, two preparations were found to contain 11·71 and 14·07 per cent. nitrogen, and melted *with charring*, at 128—129·5° and 123·5° respectively. This point requires further investigation.

Trichloromethyl-sulphonyl Thiocarbamide, $CSN_2H_3 \cdot CCl_3SO_2$ (?).

In one of the previous papers already referred to (Trans., 1886, 191), mention was made of a compound obtained along with dithiocarbamide dichloride, by the action of trichloromethyl-sulphonic chloride (2 mols.) on thiocarbamide (4 mols.) in alcoholic ethereal solution, and which was described as "crystallising in stellate groups of the finest needles, and having probably the composition

$$(CSN_2H_4)_2(CCl_3SO_2)_3."$$

This surmise was, however, wrong, the last-mentioned compound having since been otherwise prepared (see p. 666), and the two are not identical.

This reaction has since then been further investigated. If the sulphonic chloride and thiocarbamide are allowed to act on each other, as described in the above paper, the dithiocarbamide dichloride (most of which separates) filtered off, and the alcoholic ethereal filtrate evaporated to dryness *in the cold* over sulphuric acid, a dry mass evolving a little hydrochloric acid is obtained. This mass contains some free sulphur, which, together with the hydrochloric acid, must arise, in part at least, from the decomposition of some dichloride which had not separated out (*loc. cit.*). The sulphur should be extracted by carbon bisulphide, and the residual mass may then be recrystallised from absolute alcohol, rejecting the first extraction, and with no more heating than is absolutely necessary, so as to avoid decomposition and separation of sulphur. Water may be used as solvent instead of alcohol, though it is less convenient. But from neither water nor alcohol is it easy to get a pure product, as there is a tendency to decomposition while in solution, even in the cold.

A number of different preparations were analysed with the following results:—

I. 0·3786 gram gave 36·6 c.c. N at 17° and 769 mm. pressure = 11 49 per cent. N.

II. 0·2902 gram gave 27·8 c.c. N at 7° and 75·2 mm. = 11·5 per cent. N.

0·4271 gram., ignited with lead chromate and copper oxide, gave 0·1407 gram CO_2 = 8·98 per cent. C.*

III. 0·3433 gram gave 0·0634 gram H_2O and 0·1233 gram CO_2 = 2·05 per cent. H and 9 80 per cent. C.

IV. 0·2514 gram gave 0·0444 gram H_2O and 0·0870 gram CO_2 = 1·96 per cent. H and 9·44 per cent. C.

V. 0·1157 gram, ignited with lime, gave 0·1973 gram AgCl = 42·2 per cent. Cl.

This compound might, therefore, so far as analysis goes, be one of the three following:—

	No. 1. $(CSN_2H_4)_2(CCl_3SO_2)_2$.	No. 2. $CSN_2H_3{\cdot}CCl_3SO_2$.	No. 3. CSN_2H_4,CCl_3SOOH.
C........	9·28 p. c.	9 32 p.c.	9·25 p. c.
H........	1·55 „	1·17 „	1·93 „
N........	10·83 „	10·87 „	10·76 „
Cl........	41·20 „	41·36 „	41·04 „

		Found.	
C..........	8·98	9 80	9·44
H..........	—	2·05	1·96
N..........	—	11 49	11·5
Cl	—	—	42·2

In these there is no appreciable difference in the percentage of any constituent present, excepting in that of the hydrogen, and even there the differences are very slight. And further, the compound was never got sufficiently pure to allow of deciding with accuracy between such slight differences. It is, however, not No. 1, $(CSN_2H_4)_2(CCl_3SO_2)_2$, which has already been described. Neither is it No. 3,

$$CSN_2H_4,CCl_3{\cdot}SOOH,$$

which, when pure, crystallises from water and from alcohol in a totally different form, and is, besides, much more soluble in both of these liquids than this compound. The inference therefore is that it is No. 2, viz., trichloromethyl-sulphonyl thiocarbamide,

$$CSN_2H_3{\cdot}CCl_3SO_2,$$

---

* The water of this combustion was unfortunately lost.

very probably mixed with more or less thiocarbamide and trichloromethyl-sulphinate, $CSN_2H_4,CCl_3{\cdot}SOOH$,* its formation in that case being represented by the following reaction:—

$$4CSN_2H_4 + 2CCl_3{\cdot}SO_2Cl = (CSN_2H_4)_2Cl_2 + CSN_2H_3{\cdot}CCl_3SO_2 \\ + CSN_2H_4,CCl_3{\cdot}SOOH.$$

That no volatile compound is formed here, is proved by the fact that if weighed quantities of the sulphonic chloride (2 mols.) and thiocarbamide (4 mols.) are allowed to act on each other, using the least possible quantity of alcohol as solvent, the solution transferred to a large watch-glass, and the alcohol then *rapidly* evaporated over sulphuric acid in a vacuum (so as to prevent decomposition of the $(CSN_2H_4)_2Cl_2$ formed), the total weight of the products obtained is the same as that of the original compounds taken, and does not alter substantially so long as the watch-glass remains in a dry atmosphere. If, on the other hand, a smaller proportion of thiocarbamide to sulphonic chloride is taken, a very distinct loss of weight ensues, owing to the formation and volatilisation of the free sulphinic acid, $CCl_3{\cdot}SOOH$. I have not so far been able to make out satisfactorily here the formation, in the first instance, of the third product in the above equation, viz., $CSN_2H_4,CCl_3{\cdot}SOOH$, but the following consideration points to its presence.

It will be remembered that when an aqueous solution of dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$, is warmed, or has alkali added to it, it splits up according to the equation

$$(CSN_2H_4)_2Cl_2 = CSN_2H_4 + CNNH_2 + S + 2HCl.$$

It therefore occurred to me that further proof of the formation ot the above compound, trichloromethyl-sulphonyl thiocarbamide, $CSN_2H_3.CCl_3SO_2$, might be obtained by allowing weighed quantities of sulphonic chloride (2 mols.) and thiocarbamide (4 mols.) to react in a very small amount of alcohol, and then—after dilution with water—by titrating the liquid with alkali of known strength. If, in addition to the dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$, the two compounds, $CSN_2H_3{\cdot}CCl_3SO_2$ and $CSN_2H_4,CCl_3{\cdot}SOOH$, were really formed, it was probable that one of these two (the sulphinate) would be more readily decomposed by alkali than the other. As a matter of fact, on titrating *in the cold*, it is seen that the last fourth of alkali is used up much more slowly than the first three-fourths, and indeed, in one or two titrations, a sharp break seemed to occur after adding three-fourths of the total requisite alkali, the solution then remaining neutral for a short time in the cold. On warming, the neutralisation of the alkali is of course very rapid.

---

* See note on the effect of solution in ether on this compound.

There is, therefore, strong reason to suppose the foregoing compound to be trichloromethyl-sulphonyl thiocarbamide,

$$CSN_2H_3 \cdot CCl_3SO_2.$$

From alcohol, it crystallises in the finest silky needles, the whole mass looking exactly like cotton-wool. Sometimes the needles are so fine that they are only to be distinguished as such under the microscope at the edges of the round-shaped masses. From water, it also crystallises in the finest needles. It is very sparingly soluble in water, even more so than the dithiocarbamide compound, $(CSN_2H_4)_2(CCl_3SO_2)_2$, although, after once being dissolved, the crystals do not again separate out very quickly. It is moderately soluble in warm absolute alcohol, very sparingly in cold, and almost insoluble in ether. If a particle of it be placed on litmus-paper and then moistened with alcohol, the litmus is at once reddened. Its solution does *not* yield dinitrate with dilute nitric acid, nor does caustic alkali cause separation of sulphur; this proves that it is not a dithiocarbamide compound. Bromine, of course, at once precipitates the sulphonic bromide, CCl_3SO_2Br. It was never obtained sufficiently pure to allow of its melting point being determined with certainty.

University College of N. Wales, Bangor,
June, 1887.

LXVIII.—*Note on a New Class of Voltaic Combinations in which Oxidisable Metals are replaced by Alterable Solutions.*

By C. R. Alder Wright, D.Sc., F.R.S., Lecturer on Chemistry, and C. Thompson, Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

The great majority of voltaic combinations hitherto investigated, whether containing one or more fluids, possess this feature in common, that the nett chemical change taking place during their action consists of the conversion of a more or less electropositive metal into a compound thereof; in some cells, the action is one of direct synthesis, *e.g.*, where an oxide or chloride is formed by the combination of the metal with oxygen or chlorine; in others, simple displacement of hydrogen, or of another metal, from an acid or salt takes place, as in the case of the ordinary zinc sulphuric acid copper voltaic circle, and in Daniell's cell and its numerous allies; in yet others, the action is of a still more complex order, *e.g.*, Grove's cell, in which the zinc becomes zinc sulphate, whilst nitric acid is reduced; and the somewhat analogous bichromate cell, Leclanché cell, &c. Some few combinations, however, are known, in which more or less feeble currents are producible without the alteration of the metallic electrodes by corrosion or conversion into compounds, such as Grove's hydrogen and oxygen "gas battery" and analogous combinations; Becquerel's so-called "oxygen circuit" (*pile à oxygène*), with nitric acid and caustic potash as the fluids; and various somewhat analogous cells in which two dissimilar fluids, or two solutions of the same substance but of different strengths, are in contact; so that different potentials are assumed by platinum or other unattacked plates placed in the two fluids respectively, although no chemical action takes place involving the material of the plates.

On carefully considering the general character of the action taking place in lead peroxide accumulators, and in Grove's nitric acid cell and analogous combinations in which the plate acquiring the higher potential is surrounded by a so-called "depolarising" compound (such as nitric acid, chromic acid, ferric chloride, manganese dioxide, &c.), it appeared to us probable that if a plate of conducting material capable of parting with oxygen (such as compressed lead peroxide) can under suitable conditions be made to play the part of an unalterable electrode (platinum, &c.) immersed in a liquid capable of yielding up oxygen, chlorine, &c., it should conversely be possible to substitute for the oxidisable metal (zinc, &c.) of ordinary galvanic cells an unalterable electrode immersed in a fluid capable of combining with oxygen, chlorine, &c. Such a plate might be expected to be the analogue of the zinc in a Daniell cell, *i.e.*, to be the plate acquiring the lower potential. On trying experiments in this direction, we have found that this is so, and that in consequence an enormous number of novel voltaic combinations can be constructed, all of which present this feature in common, that the metal which in ordinary voltaic cells is attacked is in these cells replaced by a plate of carbon, platinum, or other conducting substance remaining unchanged, immersed in a solution of some substance capable of combining with oxygen, chlorine, &c., and opposed to a similar plate in contact with either actual oxygen, chlorine, &c., or with a compound capable of readily furnishing one of these substances by deoxidation, dechlorination, &c. In all cases as yet examined by us, the plate in contact with the oxidisable fluid acquires the lower potential, and the other plate the higher potential; *i.e.*, the former is the plate to which the "negative pole" in reference to the external circuit is attached, and the latter that with which the "positive pole" is connected.

As illustrations of this new class of cells the following combinations may be mentioned:—

A. Solution of sulphurous acid opposed to chromic liquor (potassium dichromate and sulphuric acid solution) with platinum plates: oxidation to sulphuric acid and reduction to chromium sulphate is here the chemical action taking place, and maintaining a constant current.

B. Sodium sulphite solution opposed to potassium permanganate rendered alkaline with caustic potash: sodium sulphate is here formed, with reduction of the permanganate and deposition of hydrated manganese dioxide.

C. Solution of chromium sesquioxide in caustic soda opposed to chromic liquor: oxidation to sodium chromate takes place, and reduction to chromium sulphate.

D. Solution of potassium ferrocyanide opposed to chromic liquor: ferricyanide is here produced.

E. Solution of lead oxide in caustic soda opposed to alkaline permanganate, hypochlorite, or hypobromite: oxidation of the lead monoxide to dioxide here occurs, the latter separating out in the solid form.

Obviously these are only samples out of a multitude of conceivable arrangements all based on the same general principle; in each case so long as the chemical action remains unexhausted, a steady current flows capable of doing measurable amounts of external work, *e.g.*, deposition of silver by electrolysis in a silver voltameter; the electromotive forces of these combinations are in many cases considerable, exceeding, under certain conditions, that of a Daniell cell with combination C,* and being but little lower with A, B, and D. The precise value attainable with any given combination varies to some extent with the degree of concentration of the fluids, and the nature of the electrode surface, *e.g.*, whether of polished platinum foil, a tray of platinum sponge, or a plate of gas carbon, &c.

In arranging voltaic combinations of the type now under consideration, it is obvious that inasmuch as the oxidising and oxidisable liquids will in general react on each other if allowed to intermix directly, such intermixture should be prevented by interposing a stratum of suitably chosen electrolytic fluid between the two. A convenient form of cell consists of a U-tube, the bend of which is filled with such a fluid of high density, whilst the limbs respectively contain the two principal liquids, both of somewhat less density than the intermediate solution; for example, a strong solution of caustic soda at the bend, sodium sulphite and potassium permanganate solutions being placed in the limbs; or slightly diluted sulphuric acid at the bend, with lighter sulphurous acid solution and chromic liquor in the limbs respectively. Another useful form for purposes of investigation consists of a series of three vessels (beakers, basins, &c.) of which the first and third contain the oxidisable and oxidising fluids respectively, whilst the middle one contains the intermediate electrolyte, siphon tubes, or cotton or asbestos wicks connecting the first and second, and second and third vessels respectively; for example, caustic soda solution in the middle vessel, with solutions of sodium hypobromite and of lead oxide dissolved in caustic soda in the outer vessels.

---

* A cell containing sodium sulphite opposed to chromic liquor develops under suitable conditions an E.M.F. of about 1·5 volt, or about 1·4 Daniells.

In certain cases, some interesting peculiarities appear to characterise the chemical actions taking place during the passage of the current; for example, in the case of the combination potassium ferrocyanide opposed to chromic liquor with intermediate potassium sulphate; *à priori*, two different sets of changes might be anticipated according to the view taken of the probable mechanism of the reaction. According to one view, water being regarded as the intermediary, the changes will be indicated by the scheme—

$$\begin{array}{l|l|l} K_3FeCy_6\cdot K & HO\cdot H & H_2\cdot SO_4 \\ K_3FeCy_6\cdot K & HO\cdot H & O_3\cdot Cr \\ K_3FeCy_6\cdot K & HO\cdot H & H_2\cdot SO \\ K_3FeCy_6\cdot K & HO\cdot H & O_3\cdot Cr \\ K_3FeCy_6\cdot K & HO\cdot H & H\cdot SO_4 \\ K_3FeCy_6\cdot K & HO\cdot H & \end{array}$$

$$\underbrace{\qquad\qquad}_{6K_3FeCy_6}\,|\,\underbrace{\qquad\qquad}_{6KHO}\,|\,\underbrace{\qquad\qquad}_{6H_2O}\,|\,\underbrace{\qquad\qquad}_{Cr_2(SO_4)_3},$$

so that the nett chemical change may be represented by the equation—

$$\text{(I.)}\quad 6K_4FeCy_6 + 2CrO_3 + 3H_2SO_4 = 6K_3FeCy_6 + 6KOH \\ + 3H_2O + Cr_2(SO_4)_3,$$

ferricyanide of potassium and caustic potash being formed at one side, and chromium sulphate at the other.

According to the other view, potassium sulphate being regarded as the intermediary, the changes may be indicated by the scheme—

$$\begin{array}{l|l|l|l} K_3FeCy_6\cdot K & SO_4\cdot K_2 & SO_4\cdot H_2 & H_2\cdot SO_4 \\ K_3FeCy_6\cdot K & & & O_3\cdot Cr \\ K_3FeCy_6\cdot K & SO_4\cdot K_2 & SO_4\cdot H_2 & H_2\cdot SO_4 \\ K_3FeCy_6\cdot K & & & O_3\cdot Cr \\ K_3FeCy_6\cdot K & SO_4\cdot K_2 & SO_4\cdot H_2 & H_2\cdot SO_4 \\ K_3FeCy_6\cdot K & & & \end{array}$$

$$\underbrace{\qquad\qquad}_{6K_3FeCy_6}\,|\,\underbrace{\qquad\qquad}_{3K_2SO_4}\,|\,\underbrace{\qquad\qquad}_{3K_2SO_4}\,|\,\underbrace{\qquad\qquad}_{6H_2O}\,|\,\underbrace{\qquad\qquad}_{Cr(SO_4)_3},$$

whence the nett chemical change is represented by the equation—

$$\text{(II.)}\ 6K_4FeCy_6 + 2CrO_3 + 6SO_4H_2 = 6K_3FeCy_6 + 3K_2SO_4 + 6H_2O + Cr_2(SO_4)_3,$$

differing from the former in that no caustic potash is formed along with the ferricyanide, whilst twice as much sulphuric acid becomes neutralised, half by conversion into chromium sulphate as before, and an equal amount by conversion into potassium sulphate. Of these two alternative views, the latter appears to be the more nearly correct (at any rate under certain conditions), inasmuch as practically no additional alkali was formed in a carefully conducted experiment along with the ferricyanide, whilst the quantity of acid disappearing by neutralisation corresponded approximately with that required for equation (II), and was largely in excess of that requisite for equation (I), the amount of potassium ferrocyanide converted into ferricyanide closely agreeing with the quantity calculated from the amount of silver deposited in a silver voltameter included in the circuit.

It is obvious that analogous alternative views may be held in the case of other combinations; we propose to examine certain such cases in detail, and to investigate more closely the general behaviour of cells containing oxidisable fluids, &c., instead of zinc and analogous metals, and especially the relationship between the chemical changes taking place, and the amount of electrical energy obtainable from them whilst in action.

LXIX.—*The Determination of Atomic Weights by means of the Normal Sulphate.*

By G. H. Bailey, D.Sc., Ph.D., The Owens College.

In certain groups of elements, for example, the cerium group (Ce, La, Di, Yt, Yb, Er, Sm, Sc), the magnesium-group (Cd, Be, Zn, Mg), the lead-group (Pb, Tl), two members of the tin-group (Zr, Th), and also for the non-metals sulphur and fluorine, the use of the sulphate in the determination of atomic weight constitutes either the only available method, or is at least the most trustworthy.

With some seventeen other elements, important determinations of atomic weight have been made by means of this salt, though they do not in these cases occupy so important a position as other methods which have been employed.

No further proof is needed of the necessity of making such estimations as accurate as possible, and much of the confusion which has arisen in certain of these groups may be traced to the difficulties which stand in the way of a precise measurement of the atomic weight, or what is the same thing, of the equivalent weight of the oxide. Two very considerable sources of error indeed preclude the possibility of comparing the results obtained by any two observers, or even by the same observer. The first is that there are undoubtedly differences in the character of the material used, differences which it is desirable to arrive at by definite gravimetric determinations; but in doing this we are confronted by the second obstacle which frustrates such an attempt, since there is without doubt a large variation due to the method by which such gravimetric determinations have to be made. Get rid of this manipulative error as far as possible, so that the results obtained shall be comparable, and then there will be a possibility of approaching the intricate problem of mixed oxides from this side with a fair chance of success. In the usual process by which an oxide is transformed into the normal sulphate, there are several sources which give rise to errors of unknown dimensions.

When 3 or 4 grams of a sulphate are heated for a long period at a temperature below dull redness, and then for a shorter period at dull redness, and these operations are repeated several times, there is the probability (and indeed in some cases, as we shall see, the certainty) that part of the salt is raised to the temperature of decomposition, whilst part again may not reach the temperature at which free sulphuric acid is expelled. We are thus confronted with two sources of error, of opposite sign, and of which we are ignorant of even the relative value.

Such differences vary with the time during which the experiment lasts, so that, granting even perfect manipulation, the results of two experiments would not be comparable, and unless the conditions were in all respects the same they could not be expected to agree with that approach to accuracy which is attainable by other methods. It is further manifest that dealing as we are with sources of error of opposite sign, constant weight is no sufficient guarantee of accuracy, but only an indication that a balance has been struck. This is one example of the circumstances which rob such determinations of their precision. It is true that the use of a double crucible diminishes the error from the causes mentioned, and also brings other errors, arising from the changes to which the crucible is liable, within the narrowest limits. Until, however, two factors are known, there is no certain ground for the presumption that a correct result has been obtained.

These factors are—

(*a.*) The temperature at which a sulphate gives up all the free sulphuric acid with which it may be mixed.

(*b.*) The temperature at which a normal sulphate begins to undergo decomposition.

Marignac (*Ann. Chim. Phys.* [6], 1, 289) has, indeed, rejected the determination of the atomic weight of zinc by the conversion of oxide into sulphate because he was convinced that partial decomposition of the sulphate had taken place during the process of expelling free sulphuric acid. Baubigny (*Compt. rend.*, **97**, 854, *et seq.*), conscious of the same difficulty, attempted to overcome it by using a sulphur-bath for the operation. This, however, though it may answer in certain cases, does not in any sense satisfactorily meet the objections, for, in the first place, the temperature of decomposition of the sulphate may (and in some cases certainly does) fall below 448°, and the establishment of constant weight at one given temperature does not necessarily prove anything more than that at that particular temperature, after a certain lapse of time, a state of equilibrium is set up.

Baubigny (*loc. cit.*) heated copper sulphate for three hours in the sulphur-bath, and then found that no further alteration of weight was produced by heating for ten hours at the same temperature.

Similarly he heated zinc sulphate seven hours, and then found that for the next eight hours it remained constant. Before the method of determining the atomic weight from the normal sulphate can be considered satisfactory, therefore, the temperature limits already spoken of must be known. For instance, if it be found that a sulphate gives up free sulphuric acid at 350°, and begins to decompose at 450°, it will be sufficient in all determinations to heat at some temperature sufficiently removed from these limits (say 400°) till the weight is constant. With these precautions, the determination would be received with as much confidence as determinations by other methods.

To obtain the requisite information, it was necessary to heat the salt containing excess of sulphuric acid at say 350° as long as any decrease in weight was observed, then to heat at successive temperatures, each about 10° higher, for several hours, weighing after each operation. In this way, a range of temperature was found within which no variation of weight occurred, and ultimately a point was attained at which further decrease of weight took place, indicating that the normal salt was beginning to part with its sulphuric acid. To carry this out, a form of apparatus was necessary by which it should be possible readily to keep the salt at definite and successively increasing temperatures for a considerable time. This consisted essentially of a heating tube (*Chem. News*, **54**, 302) mounted horizontally in a furnace heated by Bunsen burners, the tube inclosing an air thermometer, and a narrower tube into which the substance to be experimented upon was introduced in a platinum boat. The air thermometer served not only to measure the temperature, but in combination with a column of mercury in a U-tube, also acted as a gas regulator. The lesser tube containing the platinum boat could be readily connected with a pump by which dry air could be aspirated through it in order that the salt should not be exposed in an atmosphere of the acid fumes. It was also easy by use of this accessory to pass the air so aspirated through a solution of barium chloride, and thus ascertain whether decomposition was taking place. With such an apparatus, the temperature could be estimated and easily kept within 5°. At the end of each period of heating, the platinum boat was withdrawn, cooled, and weighed, the same conditions being observed throughout the series of experiments. The salts examined were the sulphates of bismuth, sodium, lead, barium, zinc, magnesium, and didymium. The details of experiment will be given more fully in the case of the sulphate of bismuth, and only such facts quoted with regard to the remaining sulphates as may be of special interest; it being understood that the course of investigation was the same in all the cases. In each set of experiments, a determination of the atomic value has been calculated from the results. Though care was taken that the materials used were of sufficient purity for the purpose, the results are not intended to be regarded as having any pretension to the accuracy demanded in a careful estimation of atomic weight; they were intended rather to serve as a means of checking the work as it proceeded. The precautions taken and the amount of substance used in the experiments did not indeed admit of their being considered in any other light.

The Normal Sulphate of Bismuth, $Bi_2(SO_4)_3$.—On heating bismuth trioxide with pure concentrated sulphuric acid, a clear solution is obtained. When this is allowed to cool under such conditions that the sulphuric acid does not take up moisture from the air, a beautifully crystalline product separates.

The sulphuric acid was decanted and used to dissolve a fresh portion of the oxide. The sulphate so obtained was purified by repeated crystallisation from hot sulphuric acid. A portion of the sulphate was placed in a platinum boat and introduced into the heating tube, and as in this experiment the object was to ascertain the temperature limits spoken of above, it was advisable not to take too large a quantity for this experiment. The results were as follow :—

Bismuth sulphate heated at 340° weighed 0·7253 gram.

„	„	3	hrs. longer at	345°	0·7223	gram.
„	„	3	„	345	0·7223	„
„	„	3	„	365	0·7222	„
„	„	5	„	386	0·7223	„
„	„	5	„	405	0·7224	„
„	„	9	„	435	0·7148	„

Thus the salt up to 405° remained quite constant within the error of experiment, but at 435° it lost 0·0076 gram in the course of nine hours. At 345°, therefore, normal sulphate of bismuth gives up the excess of free sulphuric acid, and between 405° and 435° decomposition of the salt commences.

When 0·5932 of the sulphate was ignited there remained 0·3891 oxide; this result gave as the atomic weight of bismuth 204·44, a value which was manifestly too low. Although no very accurate result could be anticipated from so small a quantity of the substance, the difference was greater than might be expected on this ground. It was found, in point of fact, that when the oxide was ignited in the blowpipe a loss occurred through volatilisation, and in the course of heating this amounted to several milligrams. On the other hand, if the substance was kept below the point of fusion, it retained sulphuric acid; thus 2·1755 grams of the sulphate exposed to the flame of a good Bunsen burner for 40 hours lost weight during the whole time, but even at the end of this time, when the variation was less than a milligram after three hours' heating, there remained still 0·0318 gram of SO$_3$. The sulphuric acid, indeed, was got rid of a little above the point of fusion, but loss of oxide through volatilisation ensued if the temperature was kept sufficiently high to ensure the complete decomposition of the sulphate. Deville has indeed noticed that zinc oxide dissociates and loses weight at high temperatures, and Cooke, in his determination of the atomic weight of antimony, records that silver is volatilised, even below its melting point.

The volatility of oxide of bismuth and the loss likely to accrue in consequence, has, as far as I know, not been noticed, and hence those determinations in which it has been overlooked cannot be received with confidence.

Löwe (*Zeit. anal. Chem.*, 22, 495) for instance estimated the atomic weight by conversion of the metal into the oxide, fusing the oxide in a platinum vessel. Although, therefore, the direct conversion of sulphate into oxide is desirable from its simplicity, it cannot be used in such cases, and the relation of sulphate to oxide must be ascertained by precipitation.

A second and larger portion was now taken, and heated with the following results:—

After	8	hours		at	360°	weighed	2 2189	grams.
„	3	„	longer	„	376	„	2·2186	„
„	2	„	„	„	405	„	2·2185	„
„	4	„	„	„	418	„	2·2165	„

The point of decomposition is in this case more nearly approximated, and falls therefore between 405° and 418°, and it was not considered necessary to attempt to fix it with any greater degree of precision. We may take it that sulphate of bismuth may be safely heated as high as 405°, beyond this there is risk of decomposition. A determination of sulphuric acid gave for 2·2155 grams of the sulphate 1·4615 grams of oxide, and the atomic weight of bismuth calculated from these results is 208·33. A third series of experiments was made under like conditions, the respective weights of sulphate and oxide being 1·5635 grams and 1·0267 grams, giving an atomic weight of 208 43.

The sulphate retains its crystalline character even after heating, and does not very readily take up moisture from the air, indeed 1·5566 gram exposed for a quarter of an hour increased only half a milligram in weight. All the weighings were made, however, with the platinum boat enclosed within a tube, so as to avoid any error arising from this cause, and correction was made for displacement of air, with allowance for variation of temperature and pressure.

Zinc Sulphate.—The zinc sulphate used was prepared by dissolving the purest obtainable zinc in pure dilute sulphuric acid, leaving about one-third undissolved. The solution was concentrated and allowed to crystallise, and then recrystallised. The investigations on this salt were carried out in precisely the same manner as in the previous case. With 2·253 grams of the salt successively heated at 359°, 394°, and 410° for 22 hours, the extreme variations did not exceed half a milligram. When the temperature was allowed to rise to 427°, there was a loss amounting to 0·0018 in the course of four hours, and with a further rise of temperature the loss was of course greater. The salt which had undergone partial decomposition was now treated with excess of sulphuric acid, and again exposed for several hours to a temperature of 360°. It was found to have returned almost exactly (difference two-tenths of a milligram) to its original weight, and behaved on further heating exactly as the normal salt had done. The relation of sulphate to oxide was determined by igniting it over the blowpipe till the weight was constant. By this method, 1·2795 gram of the sulphate yielded 0·6443 gram of the oxide, corresponding to an atomic weight of 65·05. A determination was also made on a second portion by precipitation with barium chloride, the value obtained for the atomic weight being in this case 64·96. Marignac's objection to the determination of the atomic weight of zinc from the normal sulphate, using the ordinary method, is therefore a perfectly valid one, and applies equally to bismuth, for there can be no doubt that the temperature 410°, at which approximately decomposition sets in with these salts, is exceeded under the conditions which are usually observed in such estimations. On the other hand, the use of a sulphur bath as suggested by Baubigny, is not admissible in these cases. It is indeed quite possible that if the heating takes place in a vessel to which air has not free access, the decomposition will not proceed so readily, but then it is essential that such a condition should be avoided, and the sulphuric acid removed from the atmosphere surrounding the salt.

Magnesium Sulphate.—In this case, the normal sulphate gave up all free sulphuric acid at 360°, and though heated for long periods at successive temperatures up to 450°, no sensible alteration of weight occurred. The relation of sulphate to oxide was determined by igniting the sulphate, and the result checked by precipitation with barium chloride. The last portion of the sulphuric acid is retained with great tenacity, and even on long ignition and when the weight remained constant a trace of sulphuric acid was still present, and this accounts no doubt for the value obtained, 24·84, for the atomic weight, being somewhat high. The determination of this relation by simple ignition cannot therefore be safely recommended.

The sulphates of lead and barium were also examined, and were found to give the normal sulphate on heating at 360°, whilst decomposition of the sulphate did not take place even at 500°. The immediate object of the experiments being to ascertain whether a sufficient range of temperature exists during which the salt is stable, it was considered amply sufficient to extend observations to 500°.

Didymium Sulphate.—In an investigation of this nature, it was certainly of interest to examine the behaviour of one of the group of cerium metals. The material used for the preparation of the didymium salt had been prepared by myself from cerite. It had been carefully freed from cerium, erbium, yttrium, and lanthanum, but contained a small quantity of samarium, no attempt having been made to separate this body. The sulphate was made into a paste with sulphuric acid, and heated at 360°. In the cases previously cited, the sulphate under these circumstances soon became constant in weight, and remained so, but with the didymium sulphate this was only approximately the case. An approach to a constant weight was manifest, but variations amounting to a milligram or more occurred, and with each successive increase of temperature the loss was accelerated. No range of temperature could be found within which the salt remained perfectly constant. Thinking this might be due to the presence of a little oxalate, the salt was treated a second time with excess of sulphuric acid strongly heated, and then again introduced with excess of sulphuric acid into the heating apparatus. The same phenomena were, however, repeated. In this case, therefore, it seems that some modification must be made in the method if it is to give trustworthy results, and differences in the determinations of the atomic weight of didymium hitherto made are probably not entirely attributable to the variable character of the oxides employed, but due also to the readiness with which decomposition of the sulphate takes place. Whether the other earths of this group show similar variations remains to be seen. Possibly if the heating is done under reduced pressure, a range of temperature may be obtained even in this case. Of this, however, I am not able to speak at present.

In determinations of the atomic weight of the elements named at the outset of this paper, it is believed that precision may be introduced by the use of the precautions suggested, and under such conditions the accuracy attainable should be of a much higher degree than has hitherto been the case. It only remains to be mentioned that in the calculations that have been made in the course of the paper, the atomic weight of oxygen has been taken as 15·96, and that of sulphur as 31·984.

LXX.—*The Action of Acetyl Chloride on Acetoximes.*

By VICTOR MEYER, Ph.D., and ARTHUR W. WARRINGTON, B.Sc.

INVESTIGATIONS of the action of acetyl chloride on the aldoximes and acetoximes have yielded many interesting results. Most aldoximes, when treated with this reagent, yield nitriles, according to the general equation—

$$RCH : N{\cdot}OH = RC : N + H_2O.$$

Most acetoximes, on the other hand, yield acetates of the general formula—

$$R_2C : N{\cdot}O{\cdot}C_2H_3O.$$

Westenberger has shown, however, that the aldoxime obtained from terephthalic aldehyde is an exception to this rule, for, on treatment with acetyl chloride, it yields a very stable aceto-derivative. Further, camphoroxime was found by E. Nägeli (*Ber.*, **17**, 806) not to yield an acetate, as might have been expected, but, like most aldoximes, an anhydride, which H. Goldschmidt and Zurrer (*Ber.*, **17**, 2071) showed to be the nitrile of campholenic acid. The latter fact can only be explained by supposing that camphor, as an additive product of the benzene series, contains hydrogen-atoms which resemble those of the aldehydes and aldoximes in the particularly exposed positions which they occupy.

Now, the question suggested itself whether terephthalic aldoxime and camphoroxime are the only exceptions to the above rules, or whether other aldoximes and acetoximes behave in an analogous fashion.

F. Münchmeyer (*Ber.*, **20**, 507), at the request of one of us, investigated the action of acetyl chloride on isophthalic aldoxime, and obtained not an acetate, as is the case with terephthalic aldoxime, but metadicyanobenzene; a difference in the behaviour of two such similar bodies which is at present quite inexplicable.

In order to obtain a compound analogous to camphoroxime, and yet having a known constitutional formula, we prepared diisopropyl acetoxime—

$$(CH_3)_2CH{\cdot}C(N{\cdot}OH){\cdot}CH(CH_3)_2.$$

This acetoxime contains two tertiary hydrogen-atoms, one on each side of the isonitroso-group. Richard Meyer has shown how readily tertiary hydrogen-atoms are attacked; and their position seems to us quite comparable with that of hydrogen-atoms added to the benzene-ring.

Diisopropyl Acetoxime.

Diisopropyl acetoxime was prepared in the following manner:—25 grams of hydroxylamine hydrochloride and an excess of caustic potash were dissolved in a mixture of equal volumes of water and alcohol, and the solution poured into a flask containing 25 grams of diisopropyl ketone (prepared by the distillation of calcium isobutyrate). The flask was then connected with a reflux condenser, placed in a water-bath, and the contents heated for eight hours. The alcohol was then evaporated, the residual liquid diluted with water, and the acetoxime extracted with ether. After drying, the ether was distilled off and the oil remaining behind was purified by distillation.

$$[(CH_3)_2CH]_2CO + H_2N{\cdot}OH = [(CH_3)_2CH]_2C{:}N{\cdot}OH + H_2O.$$

Obtained in this way, diisopropyl acetoxime is a colourless liquid, having a strong and characteristic odour. It boils between 181°

and 185°, crystallises in melting snow, and melts between +6° and +8°.

0·1555 gram acetoxime gave 14·4 c.c. N. $t = 18·5°$. $P = 748$ mm.

	Calculated.	Found.
N	10·85	10·48

Action of Acetyl Chloride on Diisopropyl Acetoxime.

The action of acetyl chloride on diisopropyl acetoxime differs according as the temperature is kept low or allowed to rise. In the former case, part of the acetoxime is attacked and an acetate is formed; in the latter, a substance is obtained which, on treatment with water, yields a crystalline compound, isomeric with the acetoxime.

If the acetoxime is added cautiously, drop by drop, from a separating funnel, to a large excess of acetyl chloride, and, as soon as all the acetoxime has been added, the liquid is poured into a mixture of ice and water, an oil will rise to the surface, having a pleasant ethereal odour, and resembling that to be described in connection with dipropyl acetoxime.

If, however, instead of pouring the liquid into ice and water, the excess of acetyl chloride be driven off at 100°, and the residue heated for some time on the water-bath, the acetate is converted into a thick syrup, which is completely and readily soluble in water. When the aqueous solution of this substance is treated with an excess of strong caustic potash, an oil of an intense alkaloïdal odour rises to the surface. The examination of this oil has yielded interesting and unexpected results. It has not a constant boiling point, and yet suffers but little decomposition on distillation. On standing, crystals separate from the oil; the separation of these crystals is favoured by spreading out the oil on large glass dishes. The whole mass seems to solidify, but on filtration a considerable quantity of the oily mother-liquor is obtained. If the mother-liquor is again spread out more crystals separate. By repeating this operation, we succeeded in converting nearly all the oil into crystals; these were pressed between filter-paper, and crystallised out of lukewarm water.

To our astonishment, the pure crystals had not the faintest odour. The intense alkaloïdal odour must be ascribed therefore not to the crystals, but to the oil, the last trace of which had only been removed by the recrystallisation.

The new compound possesses exceedingly interesting properties. It forms beautiful, colourless, transparent needles, which are very soluble in ether and alcohol, and quite soluble enough in water for the purpose of recrystallisation. It is very volatile; like naphthalene, it sublimes at the ordinary temperature of a room. It melts at 102°, and distils without the slightest decomposition at 210°.

Analysis gave the following results:—

I. 0·1587 gram substance gave 15·2 c.c. N. $t = 21°$ C. P = 742·5 mm.

II. 0·1344 gram substance gave 12·2 c.c. N. $t = 17°$ C. P = 754·5 mm.

III. 0·2186 gram substance gave 0·5198 gram CO_2 and 0·2301 gram H_2O.

	Calculated for $C_7H_{15}NO$.	Found. I.	II.	III.
C..........	65·12	—	—	64·94
H..........	11·63	—	—	11·74
N..........	10·85	10·65	10·53	—

These numbers show that the new substance and the acetoxime used in its preparation, although their properties are so different, have, nevertheless, the same percentage composition. The vapour-density of the new compound as determined in thymol vapour by C. and V. Meyer's method, gave results showing that its molecular weight also is identical with that of the acetoxime.

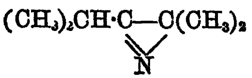
I. 0·0464 gram substance displaced 8·8 c.c. air. $t = 24·5°$. P = 741·3 mm.

II. 0·508 gram substance displaced 9·8 c.c. air. $t = 24·5°$. P = 741·3 mm.

III. 0·0396 gram substance displaced 7·55 c.c. air. $t = 24·5°$. P = 741·3 mm.

Vapour-density calculated for $C_7H_{15}NO$.		Vapour-density found.
4·47	I........	4·70
	II........	4·62
	III........	4·67

What is the constitutional formula of the isomeride? It was thought that, as in the case of camphoroxime and of most aldoximes, the acetyl chloride had acted as a dehydrating agent, and that a compound having the following structural formula had at first been formed:—



$$(CH_3)_2CH{\cdot}C\text{—}C(CH_3)_2 \atop \diagdown N \diagup$$

This would be a "metanitrile." But as metanitriles are very unstable, it might be supposed that this hypothetical product recombined with water, and yielded—

$$(CH_3)_2CH\cdot C(NH)\cdot C(CH_3)_2\cdot OH.$$

But the isomeride yielded no salts. Although it dissolved in acids, and on the addition of alkalis it readily separated out again, it did not yield any definite compound with hydrochloric acid, platinum tetrachloride, or sulphuric acid. An attempt was made to detect the presence of the imido-group by means of nitrous acid, but no nitroso-derivative could be obtained.

Its constitution was at last ascertained by a study of the products of its decomposition on continued boiling with concentrated alcoholic potash, or by heating it with concentrated hydrochloric acid in a closed tube. By either of these means it suffered decomposition, yielding only isobutyric acid and isopropylamine. After decomposition by hydrochloric acid, the isobutyric acid was driven over with steam, converted into the barium salt, and analysed.

0·3405 gram of the Ba salt dried at 150°* yields 0·2574 gram $BaSO_4$.

	Calculated for $(C_4H_7O_2)_2Ba$.	Found.
Ba	44·07	44·43

A small portion of the calcium salt was prepared. It was more soluble in hot than in cold water, and must therefore have been a salt of isobutyric and not of butyric acid.

The isopropylamine was converted into the platinochloride, the analysis of which gave the following numbers:—

0·5988 gram platinochloride gave 0·2260 gram platinum after ignition.

	Calculated for $((CH_3)_2CH\cdot NH_2)_2,H_2PtCl_6$.	Found.
Pt	37·74	37·17

This decomposition, taken together with the results obtained by Ernst Beckmann (*Ber.*, **19**, 992), in a recent investigation of the action of phosphorous pentachloride on diphenylacetoxime, leaves scarcely a doubt as to its constitutional formula. Beckmann, by the action of phosphorous pentachloride on diphenylacetoxime, obtained a chloride, $(C_6H_5)_2CNCl$, which on treatment with water yielded, not the original acetoxime as might have been expected, but an isomeride. The chlorine had changed place with the phenyl group.

---

* According to Fittig (*Ber.*, 13, 1316), barium isobutyrate crystallises with ½ mol. H_2O, which it loses at 150°.

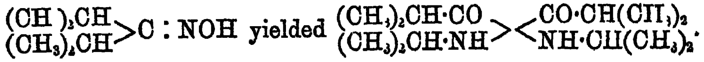
$$(C_6H_5)_2C:N{\cdot}OH + PCl_5 = C_6H_5{\cdot}CCl:N{\cdot}C_6H_5 + HCl + POCl_3.$$

This chloride Beckmann identifies beyond a doubt with one discovered by Wallach (*Annalen*, **184**, 1). On treatment with water, it yielded benzanilide,

$$C_6H_5{\cdot}CCl:N{\cdot}C_6H_5 + HOH = C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + HCl.$$

In a similar manner, in diisopropyl acetoxime, the chain of carbon-atoms had been broken and relinked by nitrogen. Diisopropyl acetoxime had yielded

Isopropylamide of isobutyric acid, the compound we have been describing.



$$\begin{matrix}(CH_3)_2CH\\(CH_3)_2CH\end{matrix}\!>C:NOH \text{ yielded } \begin{matrix}(CH_3)_2CH{\cdot}CO\\(CH_3)_2CH{\cdot}NH\end{matrix}\!>\!<\!\begin{matrix}CO{\cdot}CH(CH_3)_2\\NH{\cdot}CH(CH_3)_2\end{matrix}.$$

As we have shown, the ether,

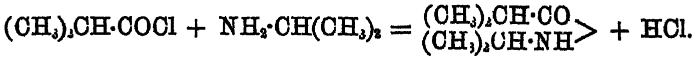
$$(CH_3)_2CH{\cdot}C(N{\cdot}O{\cdot}C_2H_3O){\cdot}CH(CH_3)_2,$$

is at first formed, but what is the nature of the further reaction which takes place, resulting in the formation of isobutyryl-isopropylamine, we do not know.

If the above views concerning the constitution of the isomeride be correct, it should be easy to prepare it synthetically from isobutyryl chloride and isopropylamine. This we succeeded in doing.

The isobutyryl chloride necessary for this purpose was obtained from Kahlbaum, and the isopropylamine made by the reduction of ordinary acetoxime, according to the method lately published by H. Goldschmidt (*Ber.*, 19, 3232).

An ethereal solution of isopropylamine combines with isobutyryl chloride to form a compound, which is identical with that obtained from diisopropylacetoxime in appearance, solubility, melting point, and chemical properties.



$$(CH_3)_2CH{\cdot}COCl + NH_2{\cdot}CH(CH_3)_2 = \begin{matrix}(CH_3)_2CH{\cdot}CO\\(CH_3)_2CH{\cdot}NH\end{matrix}\!> + HCl.$$

Thus the question of the constitution of this compound may be considered settled.

It has been observed that, besides the crystals of isobutyryl isopropylamine there was also an oil formed by the action of acetyl chloride on diisopropyl acetoxime; this oil possesses an intensely alkaloidal smell, and is possibly a derivative of pyridine. The nature of this oil will be the subject of further investigation.

Dipropyl Acetoxime.

Dipropyl ketone, prepared by the distillation of calcium butyrate, was treated with hydroxylamine like the iso-compound.

The dipropyl acetoxime obtained was purified by distillation. It is a colourless liquid, boiling between 190° and 195°, and it does not solidify in a freezing mixture.

0·2059 gram yielded 19·7 c.c. N. $t = 15°{\cdot}5$ C. $P = 746{\cdot}3$ mm.

	Calculated.	Found.
N	10·85	10·92

Action of Acetyl Chloride on Dipropyl Acetoxime.

In whatever way dipropyl acetoxime was treated with acetyl chloride, it always yielded an acetate. By allowing the acetoxime to drop into an excess of acetyl chloride, and boiling the mixture, in connection with a reflux condenser, all the acetoxime was converted into the acetate. After boiling, the mixture was poured into cold water. An oil of very pleasant odour rose to the surface; this was extracted with ether, the ether evaporated at about 50°, and the oil allowed to stand in a vacuum over sulphuric acid for several hours.

0·2720 gram gave 18·5 c.c. N. $t = 16°$. $P = 752$ mm.

	Calculated for $C_3H_7{\cdot}C(N{\cdot}O{\cdot}C_2H_3O){\cdot}C_3H_7$.	Found.
N	8·00	7·91

In conclusion, it may be stated that it seems that a reaction similar to the one by which isobutyryl isopropylamine was obtained from diisopropyl acetoxime, only takes place when the acetoxime contains a tertiary hydrogen-atom.

Methylisopropyl acetoxime and phenylisopropyl acetoxime (Rattner, *Ber.*, **20**, 506),

$$(CH_3)_2CH{\cdot}C(NOH){\cdot}CH_3 \text{ and } (CH_3)_2CH{\cdot}C(NOH){\cdot}C_6H_5,$$

each containing a tertiary hydrogen-atom, behave like diisopropyl acetoxime when treated with acetyl chloride, while the acetoximes of benzophenone and acetophenone,

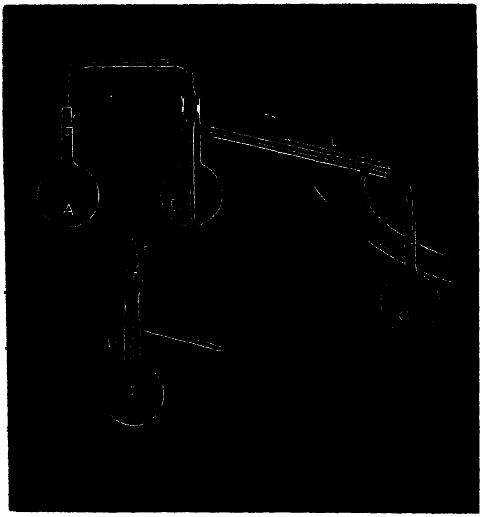
$$C_6H_5{\cdot}C(NOH){\cdot}C_6H_5 \text{ and } C_6H_5{\cdot}C(NOH){\cdot}CH_3,$$

which do not contain tertiary hydrogen-atoms yield ethers when treated with acetyl chloride, as has been shown by E. Spiegler and Rattner respectively.

LXXI.—*Note on an Improved Form of Apparatus for the Separation of Iodine, Bromine, and Chlorine.*

By M. Dechan, F.C.S.

In a paper read before the Chemical Society last year (Trans., 1886, 682), I gave a detailed description of a new method for the separation of the halogens iodine, bromine, and chlorine. In the apparatus figured in the paper above referred to, the use of cork fittings was a serious source of error, unless guarded against, as both the iodine and bromine readily attack cork. In consequence of this, nothing like accurate results could be obtained until the exposed surface of the cork became saturated with the bromine and iodine. With the view of eliminating this source of error, I have had the apparatus, of which a sketch is given below, specially constructed. In the improved apparatus, the use of cork is entirely dispensed with, the tubes being accurately ground to fit the distilling flask. I have also improved the arrangements so that a current of steam may be passed through the liquid undergoing distillation. This shortens very considerably the time necessary to complete the operation.



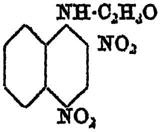
The apparatus, D, F, is that used when the distillation is performed in the ordinary manner. The arrangement, A, D, L, C shows the apparatus fitted up so that the distillation may be conducted with the aid of a current of steam. The flask D should have a capacity of about 200 cc.

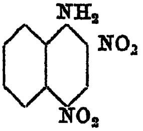
LXXII.—*Notes on Anhydro-bases. I. Ethenyltriamidonaphthalene.*

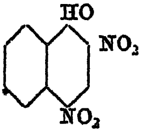
By Raphael Meldola, F.R.S., and F. W. Streatfeild, F.I.C.

When α-acetnaphthalide is warmed in glacial acetic acid solution with the necessary quantity of fuming nitric acid (2 mols. HNO_3), a dinitro-derivative is obtained which on boiling with alkalis furnishes dinitro-α-naphthol (Liebermann and Hammerschlag, *Annalen*, **183**, 272). The dinitronaphthylamine corresponding to these compounds is known to have the amido-group and one nitro-group in the homonucleal α-positions, and the other nitro-group in the homonucleal β- (ortho) position with respect to the NH_2-group (Worms, *Ber.*, 1882, 1813). This constitution is further established by the fact that the elimination of the NH_2-group by the diazo-reaction gives rise to the formation of a dinitronaphthalene (m. p. 144°) which when reduced yields a naphthylenediamine having all the characters of a meta-compound (Urban, *Ber.*, 1887, 973). Although the constitution of these compounds is thus definitely settled, it seemed advisable to take advantage of the possession of a considerable quantity of dinitro-α-acetnaphthalide, which had been prepared in the course of former investigations, in order to give additional support to the established view of the relative positions of the substituents in this compound.

Admitting the generally received formula as correct, it might be expected that on complete reduction an anhydro-base would be obtained which, as a representative of the amidated amidines, a class of compounds hitherto but little studied, might be worthy of special investigation. Our experiments have shown that such an anhydro-base is formed, and the generally received formulæ,

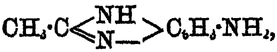






thus derive additional support, a conclusion of some interest in connection with the constitution of the naphthalene-derivatives, since a different formula has been assigned to dinitro-α-naphthol by P. Jacobson (*Inaug. Diss*, Berlin, 1882), who comes to the conclusion that the nitro-groups are in the ortho-positions, β_3, α_4.

Of amidated anhydro-bases ethenyltriamidobenzene,

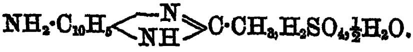


$$CH_3\cdot C\begin{matrix}\diagup NH \diagdown \\ \diagdown N\text{—} \diagup\end{matrix}C_6H_3\cdot NH_2,$$

has been investigated by Hobrecker (*Ber.*, 1872, 923) and later by Salkowski (*Ber.*, 1877, 1692). More recently ethenyltriamidotoluene has been thoroughly investigated by Niementowski (*Ber.*, 1886, 715).

In order to prepare ethenyltriamidonaphthalene, dinitro-α-acetnaphthalide was mixed with a small quantity of alcohol and then warmed with tin and concentrated hydrochloric acid. A strong reaction soon commences, and when this is over the contents of the flask are kept boiling for about two hours. The alcohol was evaporated off and the tin precipitated as sulphide, the hydrochloride of the base remaining in the solution. In our first preparations, before the properties of the hydrochloride had been studied, we found it preferable to precipitate the base in the form of sulphate, this salt being extremely insoluble and remarkably stable. On adding dilute sulphuric acid to the solution of the hydrochloride, the sulphate immediately separates in the form of a pulp of minute, white needles which are almost insoluble in cold water and alcohol, and soluble only with great difficulty in boiling water. In later preparations, when the sulphate was required, it was found that the insolubility of this salt enabled us to separate it completely from the solution directly after reduction, without the previous removal of the tin, the latter being washed out by frequently treating the mass of crystals on the filter with water. In order to purify the sulphate for analysis it was washed into a beaker and warmed with water and ammonium carbonate. The free base being readily soluble in water passes into solution, and after filtration to remove insoluble impurities, is again precipitated by dilute sulphuric acid, the sulphate being then collected and thoroughly washed with cold water. This treatment is repeated two or three times if necessary, until the sulphate dissolves in the presence of ammonium carbonate without leaving any residue.

Analyses of the sulphate showed that this salt contained water of crystallisation, and it was found that this water could not be completely driven off even at a very high temperature. Thus 0·3841 gram of one preparation heated for three hours at 220°, lost 0·0044 gram, equal to 1·14 per cent. Above 220° decomposition begins to take place This circumstance, combined with the fact that the salt also tends to retain a small quantity of moisture which is given off at a comparatively low temperature (80—91°), has rendered it somewhat difficult to fix the exact composition, but the results point distinctly to the formula—



$$NH_2\cdot C_{10}H_5\!<\!\begin{smallmatrix}N\\NH\end{smallmatrix}\!>\!C\cdot CH_3,H_2SO_4,\tfrac{1}{2}H_2O.$$

I. 0·1862 gram, allowed to dry for about two weeks in the air, gave 0·3236 gram CO_2 and 0·0718 gram H_2O.

II. 0·0674 gram, dried in a vacuum over calcium chloride, gave 0·1172 gram CO_2 and 0·0284 gram H_2O.

III. 0·1391 gram, dried as in the last preparation, gave 0·2412 gram CO_2 and 0·0552 gram H_2O.

IV. 0·1960 gram, dried as in the last preparation, gave 0·1451 $BaSO_4$.

	Calculated for $C_{12}H_{11}N_3,H_2SO_4,H_2O$.	Calculated for $C_{12}H_{11}N_3,H_2SO_4,\frac{1}{2}H_2O$.	Found.			
			I.	II.	III.	IV.
C....	46·00	47·36	47·39	47·42	47·28	—
H...	4·79	4·60	4·28	4·68	4·41	—
S....	10·22	10·52	—	—	—	10·16

The combustions were all made in a platinum boat in a current of air passing over lead chromate, the last traces of carbon being burnt by the admission of oxygen. The retention of moisture is well shown by the specimen from which the third of the above combustions was made. 0·1833 gram of this preparation, after being allowed to dry in the air for a few days, gave 0·3057 gram CO_2 and 0·0746 gram H_2O, corresponding to 45·48 per cent. C and 4·52 per cent. H. The same specimen, after drying in a vacuum over calcium chloride for some days, gave the results shown above for combustion No. III. Confirmation of these results was obtained by burning another air-dried specimen, of which 0·1597 gram gave 0·2730 gram CO_2 and 0·0642 gram H_2O, corresponding to 46·62 per cent. C and 4·46 per cent. H. This specimen on drying lost 1·3 per cent. of its weight at 80—90° in $3\frac{1}{2}$ hours (0·1762 gram lost 0·0023), the weight then remaining constant at 140—150° for two hours. The foregoing combustion, when corrected for this 1·3 per cent. of moisture, corresponds to 47·24 per cent. C and 4·52 per cent. H.

Putting the results in a tabular form for better comparison—

	Air-dried.	Corrected for 1·3 per cent. loss on drying.	Calculated for $C_{12}H_{11}N_3,H_2SO_4,\frac{1}{2}H_2O$.
C......	46·62	47·24	47·36
H......	4·46	4·52	4·60

[The carbon only need be taken into consideration, since the whole amount of hydrogen is so small that the differences may be fairly attributed to experimental error.]

The evidence is thus in favour of the formula given above, the salt containing a half molecule of water which cannot be expelled.

In order to prepare the hydrochloride, the dinitroacetnaphthalide was reduced as before, and after the removal of the alcohol by evaporation, the tin was precipitated as sulphide, and the solution containing the hydrochloride of the base evaporated to the crystallising point. The crystals, after the removal of the mother-liquor, were dissolved in a small quantity of warm water, the solution filtered and the filtrate mixed with about an equal volume of strong hydrochloric acid. On standing for a day, the pure hydrochloride slowly separated in the form of thick, stumpy needles, arranged in stellate aggregations and of a brownish colour.

I. 0·1067 gram, dried in a vacuum over calcium chloride, gave 0·1901 gram CO_2 and 0·0479 gram H_2O.

II. 0·1061 gram, allowed to dry for some days in the air, gave 0·1888 gram CO_2 and 0·0486 gram H_2O.

III. 0·1692 gram (air-dried) burnt with lime gave 0·1674 gram AgCl.

IV. 0·1725 gram (air-dried) burnt with lime gave 0·1703 gram AgCl.

	Calculated for $C_{12}H_{11}N_3,2HCl,H_2O$.	Calculated for $C_{12}H_{11}N_3,2HCl,1\frac{1}{2}H_2O$.	Found.			
			I.	II.	III.	IV.
C....	50·00	48·48	48·58	48·54	—	—
H...	5·21	5·39	4·98	5·08	—	—
Cl...	24·65	23·90	—	—	24·47	24·42

The combustions were made, as in the case of the sulphate, in a platinum boat in air and finally in oxygen, the front part of the tube being packed with lead chromate. Nos. I and II were different preparations. A remarkable circumstance in connection with this salt is the presence of a minute trace of some inorganic substance, which was invariably left in the form of ash in the platinum boat. This ash was present in all the specimens of the hydrochloride, however carefully purified by frequent crystallisation, in some instances being quite unweighable, and in others making only a difference of at most 0·2 per cent. in the carbon when the ash was weighed, and its amount subtracted from the weight of substance taken. The above analyses (I and II) were, however, made with preparations leaving no weighable amount of residue.

The above results indicate that the salt contains 1½ mol. of water of crystallisation if (as we believe must be allowed) the greatest weight is given to the carbon determinations. When heated in the air the salt loses both water and hydrochloric acid, but the residue does not appear to have any definite composition, as will be seen from the following results:—

0·1123 gram of a specimen dried at 80—90° until constant gave when burnt with lime 0·0934 gram AgCl, corresponding to 20·57 per cent. of Cl.

A further quantity of the same specimen was then heated at 110—120° until constant, when 0·1088 gram gave 0·0956 gram AgCl = 19·8 per cent. Cl.

The total loss of weight in this specimen was 22 21 per cent., being made up of 10·08 per cent. at 80—90°, and 12·13 per cent. at 110—120°. This amount of loss corresponds approximately to that required by a reduction of the salt $C_{12}H_{11}N_3,2HCl,1\frac{1}{2}H_2O$ to $C_{12}H_{11}N_3,HCl$ (calculated 21·3), but the residue, as shown by the amount of Cl, cannot have the latter formula, which requires 15 per cent. of Cl. It is not improbable that these anomalous results are due to a process of oxidation which the salt undergoes when heated in the air, and to which further reference will be made subsequently.

The above described salt was obtained, as already stated, by slow crystallisation. Having used up all our material in the course of the preceding experiments, a fresh supply of dinitroacetnaphthalide was reduced as before, and the hydrochloride prepared in the manner already described. In the course of the purification of this salt by recrystallising from hydrochloric acid, it was observed that the separation of the crystals could be promoted by scraping the sides of the beaker with a rod, or by briskly stirring the cold solution. These crystals were white needles of a greater length and more slender than the brownish, stumpy needles of the salt previously prepared, and analysis proved that they possessed a different composition, containing only a half molecule of water.

I. 0·1272 gram (air-dried) gave 0·2423 gram CO_2 and 0·0601 gram H_2O.

II. 0·1646 gram (air-dried) burnt with lime gave 0·1699 gram AgCl.

III. 0·1580 gram (dried in a vacuum over $CaCl_2$) burnt with lime gave 0·1632 gram AgCl.

	Calculated for $C_{12}H_{11}N_3,2HCl,\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
C	51·61	51·95	—	—
H	5·01	5·25	—	—
Cl	25·80	—	25·53	25·55

In order to determine the amount of water present in this salt, the drying was effected in a U-tube immersed first in a water-bath and afterwards in strong sulphuric acid, a stream of dry hydrogen being allowed to pass over the heated salt and then into Geissler bulbs containing weak alkali.

0·1928 gram, heated at 100° until constant in weight (2½ hours), lost 0·0052 gram = 2·7 per cent.

On continuing the heating at 110—120° until constant (2½ hours) the loss was 0·0066 gram = 3·42 per cent. After keeping for 2½ hours at 130—140° the loss was 0·0069 = 3·57 per cent. As the specimen seemed at this stage to have become constant in weight, the alkaline liquor in the bulbs was tested for hydrochloric acid and found to contain a trace. It appears therefore that the salt loses its water and a small quantity of its acid at the temperature employed:—

	Calculated for $C_{12}H_{11}N_3,2HCl,\frac{1}{2}H_2O$.	Found.
H_2O	3·22 per cent.	3·57

In order to ascertain whether oxidation takes place on drying in the air, as we had reason to suspect from our previous experience with the more highly hydrated salt, the current of hydrogen was replaced first by dry air and afterwards by moist air, the temperature being kept finally at 140° for three hours. The various weighings which were made from time to time showed that the salt was slowly increasing in weight, and therefore probably undergoing oxidation. The gain at the last weighing was 0·0020 gram = 1·07 per cent. upon the anhydrous salt. The alkaline liquor in the Geissler bulbs on being tested showed that hydrogen chloride was being slowly given off.

Another specimen of the hydrochloride was dried at 100° in a current of dry hydrogen until constant:—

0·1715 gram lost 0·0045 = 2·62 per cent.

This anhydrous salt gave the following results on combustion:—

0·1222 gram gave 0·2371 gram CO_2 and 0·0560 gram H_2O.

	Calculated for $C_{12}H_{11}N_3,2HCl$.	Found.
C..........	53·37	52·91
H..........	4·81	5·09

The hydrochloride is readily soluble in cold water but less soluble in hydrochloric acid solution. The neutral aqueous solution of the salt undergoes slow oxidation on exposure to the air, especially on heating, with discoloration and the separation of a white, flocculent substance. The formation of this product of oxidation takes place more rapidly when air is blown through the warm solution, a fact which was brought to light in the course of some attempts to purify the salt by saturating its aqueous solution with hydrogen chloride. The salt is more stable in the presence of excess of acid.

Stannochloride.—The hydrochloride forms a stannochloride which separates out when the product of reduction of the dinitroacetnaphthalide by tin and hydrochloric acid is evaporated to the crystallising point. It forms rosettes of white needles, but appears to be stable only in the presence of excess of stannous chloride. As soon as the latter is removed and the crystals redissolved in water or hydrochloric acid, oxidation takes place by atmospheric oxygen, the tin no doubt acting as carrier, and the white, flocculent oxidation product separates out. The salt was not therefore obtained sufficiently pure for analysis.

Platinochloride.—On adding a solution of platinic chloride to a strong aqueous solution of the hydrochloride, a dull, whitish precipitate forms, and this is shown by the microscope to consist of rosettes of needles. It dries to an ochreous, crystalline powder, which is a platinochloride of the base contaminated with a certain quantity of the product of oxidation, the platinic chloride acting as an oxidising agent, a fact shown by heating the mixed solutions before the precipitate forms when a copious separation of the white, flocculent substance takes place.

0·1079 gram gave 0·0227 gram Pt = 21·04 per cent.

The formula $C_{12}H_{11}N_3,2HCl,PtCl_4$ requires 32 39 per cent., and $(C_{14}H_{11}H_3,2HCl)_2,PtCl_4$ requires 22·4 per cent. of Pt.

Although the analysis thus favours the latter formula, we do not attach much weight to it on account of the probably impure state of the salt owing to the oxidising action of the platinic chloride already referred to.

Zincochloride.—This salt was prepared by adding a solution of zinc chloride to a strong solution of the hydrochloride and then mixing with an equal volume of strong hydrochloric acid. The salt separates in the form of white needles which become silky on drying, and gradually acquire a pinkish colour on exposure to the air. Purification was effected by simply washing the crystals on the filter with strong hydrochloric acid and finally with water. The salt was dried in a vacuum over calcium chloride.

I. 0·1248 gram gave 0·1889 gram CO_2 and 0·0511 gram H_2O.
II. 0·1226 gram burnt with lime gave 0·1503 gram AgCl.
III. 0 1389 gram, decomposed by heating with strong sulphuric acid, gave 0·0165 gram ZnO.

	Calculated for $(C_{12}H_{11}N_3,2HCl)_2,ZnCl_2,H_2O$.	Calculated for $(C_{12}H_{11}N_3,2HCl)_2,ZnCl_2,1\frac{1}{2}H_2O$.
C........	41·49	40·96
H........	4·03	4·12
Cl........	30·69	30·29
Zn........	9·36	9·24

	Found.		
	I.	II.	III.
C	41·44	—	—
H	4·57	—	—
Cl	—	30·32	—
Zn	—	—	9·53

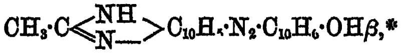
This zinc salt does not part completely with its water at 200°, the loss at this temperature being only 1·24 per cent.

We have not yet succeeded in isolating the free base, on account of its extreme solubility in water, and the tendency to oxidation which it shows in contact with the air. The solubility of the base in water is certainly a remarkable property, in view of the fact that the corresponding ethenyltriamidotoluene is almost insoluble in cold water (Niementowski, *Ber.*, 1886, 720). If the sulphate or hydrochloride is made into a paste with water and then sufficient ammonia added to combine with the acid, the free base at once dissolves and does not separate on standing; neither is it extracted from its aqueous solution by ether, benzene, or any other solvent. The aqueous solution gradually darkens and absorbs oxygen when exposed to the air, especially when warmed, but nothing separates in presence of free alkali owing to the oxidation product being of an acid character. In order to observe the formation of this product of oxidation to advantage, it is only necessary to warm a solution of the hydrochloride for a few minutes with ferric chloride, when a white, flocculent precipitate forms, and this is seen under the microscope to consist of extremely minute, white needles. The product of oxidation is distinctly acid in character, dissolving in alkalis and being reprecipitated by stronger acids; it is insoluble in water and alcohol. We have not yet obtained a sufficient quantity of the substance to enable us to determine its composition, but we propose to extend our investigations in this direction.

An attempt was made to obtain an acetyl-derivative by boiling the dry hydrochloride with sodium acetate and acetic anhydride for some hours, but no definite product was obtained, oxidation apparently taking place. Further experiments upon the acetylisation of the base will be undertaken in the course of these investigations, as the preparation of such a derivative promises to lead to interesting results in connection with the question of substitution in the second β-(homonucleal) position in the naphthalene-ring.

The NH_2-group present in the base is very readily diazotised. Thus by dissolving some of the sulphate in strong sulphuric acid, diluting with a little water and adding sodium nitrite, a solution of the diazo-sulphate was obtained which on being boiled with absolute alcohol furnished a base having all the properties of the ethenylnaphthalenediamine first obtained by P. Jacobson (*Ber.*, 1881, 1794), and afterwards more fully investigated by Prager (*Ber.*, 1885, 2161) and Lellman and Remy (*Ber.*, 1886, 799).

The diazo-salts of the base readily enter into combination with phenols, &c., giving rise to a new class of azo-colours which we propose to investigate more fully. Of these the β-naphthol compound has been prepared and examined in some detail. Its formula is doubtless—

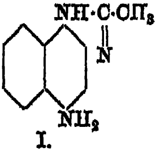


$$CH_3{\cdot}C\left\langle\begin{matrix}NH\\ N—\end{matrix}\right\rangle C_{10}H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH\beta,^*$$

although we have not yet succeeded in obtaining it sufficiently pure for analysis. The compound is thrown down as a deep violet, flocculent precipitate on mixing the solution of the diazo-salt with an alkaline solution of β-naphthol. This violet precipitate appears to be a sodium salt, as it becomes red on washing with dilute acid. The free azo-compound dries to a bronzy-looking mass having great tinctorial power. It dissolves slightly in boiling alcohol, toluene, and glacial acetic acid, more readily in boiling aniline, dimethylaniline, and phenol. Its solutions in all these solvents are of a fine red colour, but it separates on cooling in an amorphous state, and we have hitherto failed to obtain the substance in a crystalline form. It dissolves very readily in alcoholic soda or potash with a red colour, and is precipitated by acids in a red, gelatinous state. The azo-compound, especially when freshly precipitated, is freely soluble in hot aqueous alkalis, a property which is not shared by any of the non-acid azo-β-naphthol compounds, and is no doubt due to the presence of the NH-group in the anhydronaphthalene residue. It dissolves in strong sulphuric acid with a deep blue colour, becoming red on dilution.

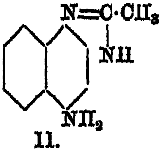
One other property of the anhydro-base deserves notice in concluding. On adding an ammoniacal solution of silver nitrate to an ammoniacal solution of the base, a white, gelatinous precipitate at once separates. This substance gradually becomes darkened on exposure to light, and on being tested was found to be a silver compound. We propose to make this the subject of further study.

With respect to the constitution of the anhydro-base two formulæ are possible:—

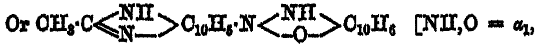


I.

or



II.



* Or $CH_3{\cdot}C\left\langle\begin{matrix}NH\\ N—\end{matrix}\right\rangle C_{10}H_5{\cdot}N\left\langle\begin{matrix}NH\\ —O—\end{matrix}\right\rangle C_{10}H_6$ [NH,O = α_1,β_2].

The recent researches of Niementowski (*Ber.*, 1887, 1874) render it most probable that the two H-atoms, which are eliminated with the oxygen of the CO·CH_3-group in the formation of anhydro-bases, are both of the same NH_2-group, and we believe therefore that the first of these formulæ is the one representing the constitution of the base forming the subject of the present paper.

Finsbury Technical College,
July 30*th*, 1887.

LXXIII.—*Dibenzyl Ether.*

By C. W. Lowe, Student in the Owens College.

Cannizzaro obtained this compound by heating benzyl alcohol with boron trioxide at 120—125° C.; he describes it as a colourless liquid, showing a faint indigo-blue fluorescence, and boiling between 310° and 315°. He further found that when heated a few degrees above 315° it assumed a yellow colour, and was resolved into toluene and benzaldehyde, a resinous hydrocarbon being formed at the same time; consequently its vapour-density could not be determined. He added that he would endeavour to confirm its formula by synthesis, according to Williamson's method; this, however, has not been done (*Annalen*, **92**, 113).

Limpricht obtained the same compound, together with anthracene and the hydrocarbon $C_{14}H_{14}$ (which afterwards was found to be benzyltoluene), by heating benzyl chloride with water at 190°. It was formed only in small quantity; he analysed it, and stated that it boiled a little above 310° (*ibid.*, **139**, 313).

Dibenzyl ether being the oxide of the most simple aromatic alcohol radicle, its further investigation appeared of interest. At the suggestion of Professor Schorlemmer, I prepared it by the action of benzyl chloride on sodium benzylate.

20 grams of sodium was dissolved in an ethereal solution of 100 grams of benzyl alcohol; heat was applied towards the end of the reaction, care being taken not to form any toluene. The white, pasty mass thus obtained was well mixed with 120 grams of benzylchloride, and gently heated in a flask provided with a reflux condenser. A rather violent reaction set in. The product, after being separated from ether and sodium chloride by distillation, was rectified over sodium and submitted to fractional distillation. It was found to

contain some toluene and benzaldehyde. By far the largest fraction, however, boiled at 295—298°, the whole mercurial column being surrounded by the vapour. The thermometer used had previously been found correct at the boiling points of water and naphthalene. As the following analyses show, this fraction consists of pure dibenzyl ether:—

	Substance.	CO_2.	H_2O.
I	0·0775	0·2400	0·0510
II	0·1615	0·5010	0·1060
III	0·1355	0·4205	0·0890

	Calculated.		Found.		
C_{14}	168	84·85	84·45	84·60	84·62
H_{14}	14	7·07	7·31	7·29	7·29
O	16	8·08	8·08	8·08	8·08
	198	100·00	99·84	99·97	99·99

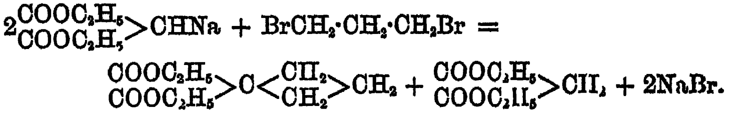
Dibenzyl ether is a colourless, very refractive liquid, without fluorescence, and having a slight but persistent odour of hawthorn blossom. It has a specific gravity of 1·0359 at 16°. The refractive index was found to be 1·5525 at the same temperature. This corresponds to a molecular refractive energy of 105·60. The calculated molecular refractive energy of dibenzyl ether is 105·4 (Bruhl, *Liebig's Ann.*, **200**, 139). On distillation, a small portion is resolved into toluene and benzaldehyde, the resinous hydrocarbon mentioned by Cannizzaro being formed at the same time, but only in minute quantity. To obtain more of it, some dibenzyl ether was heated for three or four days at a temperature of 315°, when it assumed a yellow colour and a white, flocculent substance separated out. When distilled, traces of water came over first, then toluene. The boiling point rose slowly to 132°, then rapidly to 179°, the boiling point of benzaldehyde. When this had passed over, the temperature rose to the boiling point of dibenzyl ether. A resinous residue was left behind, but the quantity was too small for analysis.

When this research was almost completed, I found that Filoti had commenced an investigation of the ethers containing aromatic alcohol radicles. Of these he has described cumyl ether, or dicymyl ether, $(C_3H_7\cdot C_6H_4\cdot CH_2)_2O$, which he prepared by the same method that I used for dibenzyl ether. This decomposes on heating into cymene and cumaldehyde (Abstr., 1884, 776; *Ber.*, **18**, Ref., 150), but the decomposition seems to occur much more readily than in the case of dibenzyl ether.

LXXIV.—*The Synthetical Formation of Closed Carbon-chains.* Part II. (continued). *On the Action of Trimethylene Bromide on the Sodium Compounds of Ethylic Acetoacetate, Benzoylacetate, Paranitrobenzoylacetate and Acetonedicarboxylate.*

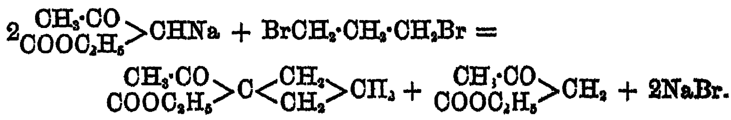
By W. H. Perkin, Jun., Ph.D.

In a paper on "Tetramethylene-derivatives," which I brought before the notice of the Society a short time since (this vol., p. 1), I showed that when the sodium-derivative of ethylic malonate is digested with trimethylene bromide, ethylic tetramethylenedicarboxylate is formed thus:—



$$2\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CHNa} + \mathrm{BrCH_2{\cdot}CH_2{\cdot}CH_2Br} =$$
$$\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CH_2} + \begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CH_2} + 2\mathrm{NaBr}.$$

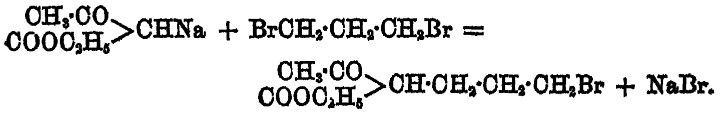
Whilst engaged on these experiments, it seemed probable that if ethylic acetoacetate or benzoylacetate were substituted for ethylic malonate, various tetramethylene-derivatives, of constitution similar to the above, might be obtained. Thus, in the case of ethylic acetoacetate, ethylic acetyltetramethylenecarboxylate should be formed:—



$$2\begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CHNa} + \mathrm{BrCH_2{\cdot}CH_2{\cdot}CH_2Br} =$$
$$\begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CH_2} + \begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CH_2} + 2\mathrm{NaBr}.$$

In a short account given of these experiments (*Ber.*, **16**, 1787), it was assumed that the products thus obtained were tetramethylene-derivatives. After careful study, however, it was found that these substances, from their decompositions and general reactions, must be quite differently constituted. The reaction between ethylic sodacetoacetate and trimethylene bromide evidently takes place in two distinct stages.

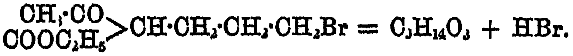
In the first place 1 mol. of trimethylene bromide reacts with 1 mol. of ethylic sodacetoacetate, forming ethylic ω-bromopropylacetoacetate, thus:—



$$\begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CHNa} + \mathrm{BrCH_2{\cdot}CH_2{\cdot}CH_2Br} =$$
$$\begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{COOC_2H_5}\end{matrix}>\mathrm{CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br} + \mathrm{NaBr}.$$

Ethylic ω-bromopropylacetoacetate.

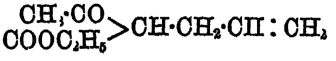
In the second phase of the reaction this intermediate product simply loses 1 mol. of hydrogen bromide, and is converted into the compound $C_9H_{14}O_3$,



$$\left.\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\right>CH\cdot CH_2\cdot CH_2\cdot CH_2Br = C_9H_{14}O_3 + HBr.$$

This change can take place in three different ways.

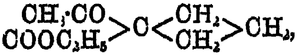
(1.) The bromine-atom can combine with the hydrogen-atom of the second CH_2-group, producing a substance of the formula



$$\left.\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\right>CH\cdot CH_2\cdot CH : CH_2$$

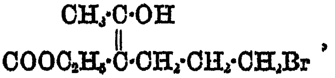
(ethylic allylacetoacetate).

(2). The bromine-atom can combine with the hydrogen-atom of the CH-group, in which case ethylic acetotetramethylenecarboxylate,



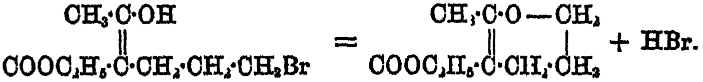
$$\left.\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\right>C\left<\begin{matrix}CH_2\\ CH_2\end{matrix}\right>CH_2,$$

would be formed; or (3) ethylic ω-bromopropylacetoacetate is first transformed into its labile form,



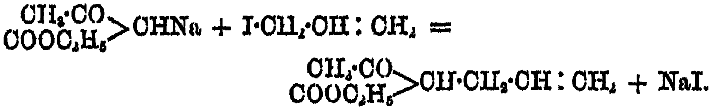
$$\begin{array}{l}CH_3\cdot C\cdot OH\\ \quad\ \ \,\|\\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\cdot CH_2Br\end{array},$$

and then hydrogen bromide is eliminated according to the equation—



$$\begin{array}{l}CH_3\cdot C\cdot OH\\ \quad\ \ \,\|\\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\cdot CH_2Br\end{array} = \begin{array}{l}CH_3\cdot C\cdot O - CH_2\\ \quad\ \ \,\|\qquad\ \ |\\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\end{array} + HBr.$$

That the substance produced in this reaction is: (1) not ethylic allylacetoacetate, is easily proved by directly comparing it with the latter compound, which can easily be prepared synthetically by treating ethylic sodacetoacetate with allyl iodide,



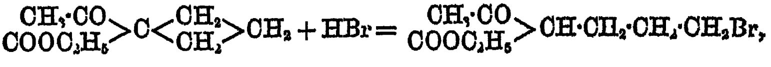
$$\left.\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\right>CHNa + I\cdot CH_2\cdot CH : CH_2 = \left.\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\right>CH\cdot CH_2\cdot CH : CH_2 + NaI.$$

The greatest differences are found to exist between the two products, as will be shown in detail further on.

That the compound $C_9H_{14}O_3$ is not ethylic acetotetramethylenecarboxylate is easily shown in the following way. If this substance be mixed with a concentrated solution of hydrogen bromide, it dissolves, and on standing is decomposed into alcohol, carbonic anhydride, and acetobutyl bromide, thus:—

$$C_9H_{14}O_3 + HBr + H_2O = \underset{\text{Acetobutyl bromide.}}{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br} + CO_2 + C_2H_5OH.$$

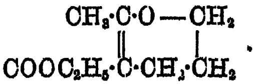
Now, if the substance $C_9H_{14}O_3$ be ethylic acetotetramethylenecarboxylate, this decomposition can only be explained on the assumption that the tetramethylene-ring is first split by the action of the hydrogen bromide thus:—



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!>\!CH_2 + HBr = \begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>\!CH\cdot CH_2\cdot CH_2\cdot CH_2Br,$$

in which case ethylic ω-bromopropylacetoacetate would first be formed, and then be further decomposed into alcohol, carbonic anhydride, and acetobutyl bromide.

It has, however, been shown (this vol., p. 6) that the tetramethylene-ring is not split even when submitted for weeks to the action of the most concentrated solution of hydrogen bromide, and it is therefore necessary to assume that the product of the action of trimethylene bromide on ethylic sodacetoacetate is not a tetramethylene-derivative, but has the constitution



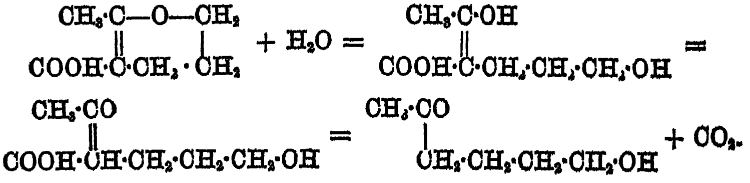
$$\begin{array}{l}CH_3\cdot C\cdot O - CH_2\\ \quad\;\;\, \| \qquad\;\; | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\end{array}.$$

This is shown still more clearly from the following decompositions.

The ethereal salt, $C_9H_{14}O_3$, when submitted to hydrolysis, is easily transformed into the corresponding acid, $C_7H_{10}O_3$. If this acid be now boiled with water for a few minutes, it is quantitatively decomposed into acetobutyl alcohol and carbonic anhydride,

$$C_7H_{10}O_3 = CO_2 + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + H_2O,$$

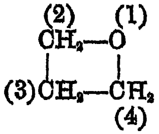
a reaction which cannot be accounted for on the assumption that the acid is a tetramethylene-derivative. If the acid, however, contain an oxygen carbon-chain, as represented above for its ethereal salt, this decomposition is very simply explained, as the acid is then simply a carboxylic acid of the anhydride of acetobutyl alcohol, and naturally is decomposed on boiling with water into this alcohol and carbonic anhydride. The reaction would then take place according to the following equations:—



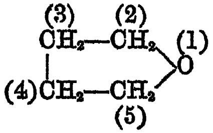
$$\begin{array}{l}CH_3\cdot C - O - CH_2\\ \quad\;\;\, \| \qquad\quad | \\ COOH\cdot C\cdot CH_2\cdot CH_2\end{array} + H_2O = \begin{array}{l}CH_3\cdot C\cdot OH\\ \quad\;\;\, \| \\ COOH\cdot C\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH\end{array} =$$

$$\begin{array}{l}CH_3\cdot CO\\ \quad\;\;\, \| \\ COOH\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH\end{array} = \begin{array}{l}CH_3\cdot CO\\ \quad\;\;\, | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH\end{array} + CO_2.$$

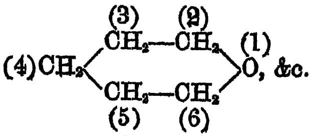
With regard to the nomenclature of these and other similarly constituted substances, I would suggest that the fully saturated oxygen carbon-rings, of which these substances are derivatives, should be named according to the following scheme:—



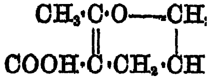
Tetrone.



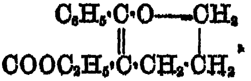
Pentone.



Hexone.

An acid of the formula  $\begin{array}{l} CH_3\cdot C\cdot O\text{—}CH_2 \\ \quad\;\;\, \| \qquad\; | \\ COOH\cdot C\cdot CH_2\cdot CH \end{array}$ would therefore be methyldehydrohexonecarboxylic acid, [2 (2, 3), 3].

In continuing this research, experiments were next made on the action of trimethylene bromide on the sodium-derivative of ethylic benzoylacetate, and it was found that in this case also tetramethylene-derivatives were not formed. The principal product of the reaction, an ethereal salt of the formula $C_{14}H_{16}O_3$, evidently has the constitution—



$$\begin{array}{l} C_6H_5\cdot C\cdot O\text{—}CH_2 \\ \qquad\;\;\; \| \qquad\; | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2 \end{array},$$

and is therefore ethylic phenyldehydrohexonecarboxylate, [2 (2, 3), 3].

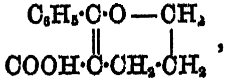
Its formation is represented by an equation similar to that given above for the formation of ethylic methyldehydrohexonecarboxylate from trimethylene bromide and ethylic sodacetoacetate. This can be proved in exactly the same way as in the case of the ethylic methyldehydrohexonecarboxylate. If the ethereal salt, $C_{14}H_{16}O_3$, be submitted to hydrolysis, it is easily converted into the corresponding acid, $C_{12}H_{12}O_3$. This acid when treated with a concentrated solution of hydrogen bromide is decomposed into carbonic anhydride and benzoylbutyl bromide,

$$C_{12}H_{12}O_3 + HBr = CO_2 + C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br,$$

and when boiled with water it yields carbonic anhydride and benzoylbutyl alcohol,

$$C_{12}H_{12}O_3 + H_2O = CO_2 + C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

reactions which are the counterpart of those which occur in the formation of acetobutyl alcohol and its bromide from methyldehydrohexonecarboxylic acid and its ethereal salt as described above. It is therefore evident that the acid, $C_{12}H_{12}O_3$, must be represented by the formula—

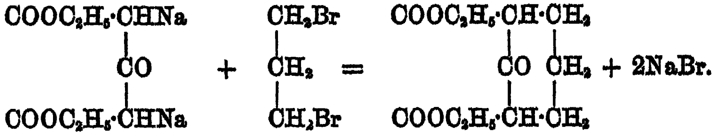


$$\begin{array}{l} C_6H_5\cdot C\cdot O - CH_2 \\ \qquad\quad \| \qquad\quad | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array},$$

and be termed phenyldehydrohexonecarboxylic acid [2, (2, 3), 3].

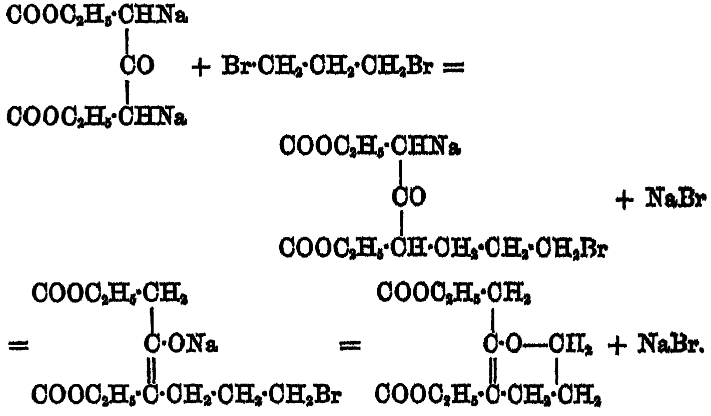
As will be shown in the experimental part of this paper, results similar to these were also obtained when ethylic paranitrobenzoylacetate was substituted in the above reaction.

Experiments on the action of trimethylene bromide on ethylic acetonedicarboxylate, which were conducted with the kind permission of Professor H. v. Pechmann, were first initiated in the hope of obtaining hexamethylene-derivatives, thus:—



$$\begin{array}{l} COOC_2H_5\cdot CHNa \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CO \\ \qquad\qquad\quad | \\ COOC_2H_5\cdot CHNa \end{array} + \begin{array}{l} CH_2Br \\ | \\ CH_2 \\ | \\ CH_2Br \end{array} = \begin{array}{l} COOC_2H_5\cdot CH\cdot CH_2 \\ \qquad\qquad\quad | \qquad | \\ \qquad\qquad\quad CO \quad CH_2 \\ \qquad\qquad\quad | \qquad | \\ COOC_2H_5\cdot CH\cdot CH_2 \end{array} + 2NaBr.$$

The further examination of the substances formed in this reaction has, however, shown that they are not hexamethylene-derivatives, but that in this case also hexone-derivatives result. It is most probable that this curious reaction takes place according to the following equation:—



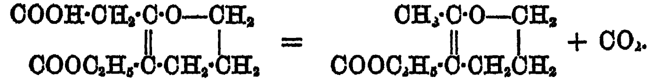
$$\begin{array}{l} COOC_2H_5\cdot CHNa \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CO \\ \qquad\qquad\quad | \\ COOC_2H_5\cdot CHNa \end{array} + Br\cdot CH_2\cdot CH_2\cdot CH_2Br =$$

$$\begin{array}{l} COOC_2H_5\cdot CHNa \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CO \\ \qquad\qquad\quad | \\ COOC_2H_5\cdot CH\cdot CH_2\cdot CH_2\cdot CH_2Br \end{array} + NaBr$$

$$= \begin{array}{l} COOC_2H_5\cdot CH_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad C\cdot ONa \\ \qquad\qquad\quad \| \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\cdot CH_2Br \end{array} = \begin{array}{l} COOC_2H_5\cdot CH_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad C\cdot O - CH_2 \\ \qquad\qquad\quad \| \qquad\quad | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2 \end{array} + NaBr.$$

The product of this reaction is therefore ethylic methyldehydrohexonedicarboxylate, [2, (2, 3), *ω*, 3]. That this is the case is easily proved in the following way:—

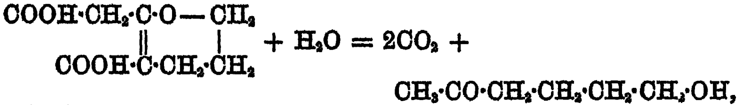
Ethylic methyldehydrohexonedicarboxylate when submitted to hydrolysis, is first transformed into its acid ethylic salt, $C_{10}H_{14}O_5$. If now this acid salt be distilled, it is decomposed into carbonic anhydride and ethylic methyldehydrohexonecarboxylate, which latter substance is identical with the compound obtained by the action of trimethylene bromide on ethylic sodacetoacetate. This interesting decomposition is clearly exhibited in the following equation :—



$$\begin{array}{l} COOH\cdot CH_2\cdot C\cdot O—CH_2 \\ \qquad\quad \| \qquad\quad | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2 \end{array} = \begin{array}{l} CH_3\cdot C\cdot O—CH_2 \\ \qquad \| \qquad | \\ COOC_2H_5\cdot C\cdot CH_2CH_2 \end{array} + CO_2.$$

Hydric ethylic methyldehydrohexonedicarboxylate.

If this hydric ethylic methyldehydrohexonedicarboxylate is treated further with alkalis, it is converted into the dicarboxylic acid, $C_8H_{10}O_5$. This dicarboxylic acid when boiled with water is easily resolved into 2 molecules of carbonic anhydride and acetobutyl alcohol, thus:—



$$\begin{array}{l} COOH\cdot CH_2\cdot C\cdot O—CH_2 \\ \qquad\quad \| \qquad\quad | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} + H_2O = 2CO_2 + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

Methyl dehydrohexonedicarboxylic acid.

a reaction exactly similar to the formation of acetobutyl alcohol, and one molecule of carbonic anhydride from methyldehydrohexonemonocarboxylic acid described above.

In the early part of this introduction it was stated that the reaction between trimethylene bromide and the various sodium compounds employed could be also explained on the assumption that allyl-derivatives were formed, and this would also explain several of the reactions of these substances. It is therefore necessary to show that these compounds are not allyl-derivatives. This is easily done by comparing first of all their physical properties with those of the allyl compounds they might be supposed to be identical with, thus :—

Melting Points.

Methyldehydrohexonecarboxylic acid	119°	Allylacetoacetic acid	Unstable.
Phenyldehydrohexonecarboxylic acid	142—144°	Allylbenzoylacetic acid	$\left\{\begin{array}{l}122°\\125°\end{array}\right\}$(?)
Ethylic methyldehydrohexonecarboxylate	+ 0°	Ethylic allylacetoacetate	Oil.
Ethylic phenyldehydrohexonecarboxylate	59—60°	Ethylic allylbenzoylacetate	Oil.
Ethylic paranitrophenyldehydrohexonecarboxylate	62—63	Ethylic allylparanitrobenzoylacetate	45—46°
Paranitrophenyldehydrohexonecarboxylic acid	172°	Allylparanitrobenzoylacetic acid	Unstable.

Boiling Points.

Ethylic methyldehydrohexonecarboxylate	226—227°	Ethylic allylacetoacetate ..	213—214°
Methyldehydrohexone	109°	Allylacetone	128—130
Phenyldehydrohexone	258—260°	Allylacetophenone	235—238

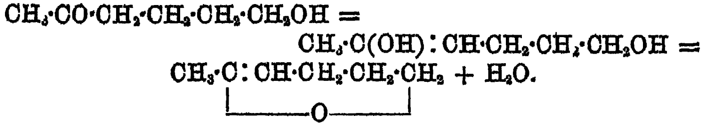
It is thus seen that these two series of substances differ most widely from each other, and cannot possibly be identical. The same differences become directly apparent on studying the chemical properties (see *Ber.*, **16**, 1797).

The careful study of the physical properties of these substances shows, however, that there are still several curious facts in connection with them which require explanation.

Thus whilst methyldehydrohexone (b. p. 109°) boils 20° *lower* than allylacetone (b. p. 128—130°), the ethereal salt of the carboxylic acid of methyldehydrohexone (ethylic methyldehydrohexonecarboxylate, b. p. 226—227°) boils 12° *higher* than the ethereal salt of the carboxylic acid of allylacetone (ethylic allylacetoacetate, b. p. 213—214°). The introduction of the same group, $COOC_2H_5$, has in the one case raised the boiling point 117°, in the other case only 84°. Again, as methyldehydrohexone boils nearly 20° *lower* than allylacetone, phenyldehydrohexone should boil at a lower temperature than allylacetophenone, but it boils 20° *higher*. It is difficult to find an explanation for these discrepancies.

The study of the magnetic rotation of these substances has also given very curious results. The magnetic rotation of methyldehydrohexone is 6·074. Now, if ethylic methyldehydrohexonecarboxylate be really the ethereal salt of the carboxylic acid of methyldehydrohexone, it should have a magnetic rotation differing from that substance by the value of the group $COOC_2H_5-H$. The value of this group is easily calculated by subtracting from the magnetic rotation of ethylic malonate (7·410) the magnetic rotation of ethylic acetate (4·462), when $COOC_2H_5-H = 2·948$. Or a value still more suited to the case in point can be obtained by deducting the magnetic rotation of acetone (3·514) from that of ethylic acetoacetate (6·501) when $COOC_2H_5-H = 2·987$. In calculating the magnetic rotation of ethylic methyldehydrohexonecarboxylate we get methyldehydrohexone (6·074) + $COOC_2H_5-H$ (2·987) = 9·061 = calculated magnetic rotation of ethylic methylhydrohexonecarboxylate. But the value actually found was 10·069, a difference of one whole number from the calculated; this is altogether unaccountable.

A further consideration which has perhaps some connection with this remarkable discrepancy is the following:—The magnetic rotation of acetobutyl alcohol is 6·502, that of its anhydride, methyldehydrohexone, is 6·074. Therefore the loss of water involved in the formation of the anhydride has reduced the magnetic rotation by 0·428. But when acetobutyl alcohol is converted into its anhydride, it is supposed that the following changes take place:—

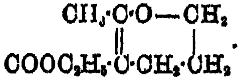


$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH = CH_3{\cdot}C(OH):CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH = \underbrace{CH_3{\cdot}C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2}_{O} + H_2O.$$

Now the diminution in magnetic rotation (0·428) can explain the dehydration which occurs, but it does not account at all for the fact that methyldehydrohexone is an unsaturated compound, in which case its magnetic rotation should be expected to be one whole number more, or about 7·074. The only theory which can be put forward at present to meet these difficulties is that methyldehydrohexone exists in two forms, namely, (α) magnetic rotation 7·074, as in ethylic methyldehydrohexonecarboxylate; and (β) magnetic rotation 6·074, as in the anhydride of acetobutyl alcohol. This would account for the high rotation of ethylic methyldehydrohexonecarboxylate which would be calculated thus: α-methyldehydrohexone (7·074) + $COOC_2H_5-H$ = (2·987) = 10·061 = calc. magnetic rotation. This agrees with the number actually found = 10·069. On distilling methyldehydrohexonecarboxylic acid, some remarkable change must take place, the α-methyldehydrohexone present in this acid being converted into the β-modification.

From these considerations it is evident that although the constitution of these various substances has been explained in a satisfactory way, from a chemical point of view, there are still several curious points of physical interest which are at present unexplained. It is hoped that further experiment will throw some light on, and afford a satisfactory explanation of these physical difficulties.

Ethylic Methyldehydrohexonecarboxylate,



$$\begin{matrix} CH_3{\cdot}C{\cdot}O-CH_2 \\ COOC_2H_5{\cdot}C{\cdot}CH_2{\cdot}CH_2 \end{matrix}.$$

In the preparation of this substance the following method has been found to give the best results:—23 grams of sodium is dissolved in 250—270 grams of absolute alcohol. To this solution of sodic ethylate, when cold, a mixture of 130 grams of ethylic acetoacetate and 105 grams of trimethylene bromide is slowly added, the whole being well cooled during the operation. The clear solution formed is then heated to boiling on a water-bath in a flask connected with a reflux condenser. In a short time the liquid becomes cloudy, owing to the separation of sodium bromide, and after about four hours' boiling, the reaction is usually at an end. In order to be sure of this, it is only necessary to mix a few drops of the solution with a little water, and test this with litmus-paper when, if the decomposition is finished, the product will show a neutral reaction. Sufficient water is now added to dissolve all the precipitated sodic bromide, and the mass is extracted about three times with ether. The ethereal solution is then well washed with water, dried over calcic chloride, and the ether distilled off. The residual slightly yellowish-coloured oil, which should weigh 140 to 150 grams, is then submitted to careful fractional distillation. The following fractions are obtained:—

100—170 = 8 grams.
170—200 = 36 ,,
200—240 = 80 ,,
Residue = 6 ,,

The fraction 170—200 consists of regenerated ethylic acetoacetate, that boiling at 200—240° contains the ethylic methyldehydrohexonecarboxylate, and gives on further fractioning 45—50 grams boiling between 216—228°. This fraction is pure enough for ordinary purposes.

Pure ethylic methyldehydrohexonecarboxylate boils at 222—223° (720 mm.) and 225—226° (760 mm.).

*Analysis gave the following results:—

I. 0·1519 gram substance gave 0·1142 gram H_2O and 0·3528 gram CO_2.

II. 0·1808 gram substance gave 0·1333 gram H_2O and 0·4201 gram CO_2.

	Theory.	Found.	
	$C_9H_{14}O_3$.	I.	II.
C........	63·53 per cent.	63·52	63·35 per cent.
H	8·24 ,,	8·35	8·19 ,,
O	28·33 ,,	28·13	28·46 ,,

A vapour-density determination in aniline vapour by Hofman's method gave—

D.....................	6·21
Theory, $C_9H_{14}O_3$	5·88

Ethylic methyldehydrohexonecarboxylate is a colourless oil having

---

* In the samples used for analysis, the slight trace of bromine which is almost invariably present in this ethereal salt when prepared as above, was first removed by treatment with zinc-dust and acetic acid.

a disagreeably penetrating, camphor-like smell. When cooled to 0° it solidifies to a white, crystalline mass which melts again at 9°. It is isomeric with ethylic allylacetoacetate which boils at 213—214° (see p. 708). As this product of the reaction of trimethylene bromide on ethylic acetoacetate was thought to be of special interest, a very pure sample was carefully prepared and submitted to physical examination. The determinations of the specific gravity and magnetic rotation of this substance, which were performed by my father, gave the following results :—

I. Sp. gr. determinations

Preparation I.	Preparation II.
$d^{15°}_{15°} = 1·06457$	$d^{15°}_{15°} = 1·06840,$
$d^{25°}_{25°} = 1·05840$	$d^{20°}_{20°} = 1·06470,$
	$d^{25°}_{25°} = 1·06137.$

Magnetic Rotations. I.

t.	Sp. rotation.	Mol. rotation.
15·0	1·1512	10·212
15·2	1·1473	10·178
15·2	1·1465	10·172
15·6	1·1472	10·180
15·8	1·1450	10·167
12·0	1·1561	10·240
12·0	1·1531	10·212
12·0	1·1517	10·200
14·1	1·1498	10·195

Magnetic Rotations. II.

t.	Sp. rotation.	Mol. rotation.
20·4	1·1419	10·130
18·8	1·1399	10·102
18·8	1·1424	10·125
18·8	1·1429	10·129
16·7	1·1448	10·127
16·7	1·1438	10·123
16·7	1·1444	10·128
18·1	1·1428	10·123

Dr. Gladstone has kindly determined the refraction equivalent of these preparations, together with that of the isomeric ethylic allylacetoacetate. He gave me the following account of his results:—

Preparation I.

	Temp.	μ_A.	μ_D.	μ_H.	Specific refraction.	Specific dispersion.	Refraction equivalent.
Ethylic methyldehydrohexonecarboxylate	13	1·4743	1·4818	1·5078	0·4446	0·0314	75·58
Ethylic allylacetoacetate..........	13·5	1·4356	1·4410	1·4598	0·4383	0·0210	74·51

"If we take Landolt's values for the three elements, $C_9H_{14}O_3$ should be 72·2. Now bodies belonging to the allyl series are about 2·0 above normal, which fairly accounts for the value of ethylic allylacetoacetate. The ethylic methyldehydrohexonecarboxylate is evidently of higher refraction and much higher dispersion, suggesting the presence of a still larger proportion of carbon in a highly refracting condition."

Preparation II.

t.	Sp. gr.	μ_A.	μ_D.	μ_H.	Observed.		Calculated.	
					Ref. eq. A.	Disp. eq. H − A.	Ref. eq. A.	Disp. eq. H − A.
24·5	1·0605	1·4607	1·4772	1·5038	75·20	5·30	72·2	3·26

"This agrees substantially with the previous specimen both in refraction and dispersion. The figures are very high, and I do not know how to interpret them."

In spite of the close agreement in magnetic rotation of these two preparations, it was thought, for reasons which are explained in the introduction (p. 708), that these numbers must still be considerably too high, and that the substance prepared in this way was not pure enough for physical measurements.

A very pure sample of ethylic methyldehydrohexonecarboxylate was therefore prepared from the silver salt of the acid by means of ethyl iodide. In doing this 50 grams of ethylic methyldehydrohexonocarboxylate (b. p. 224—228°) were hydrolysed by boiling for four hours on a water-bath with 40 grams of pure potash dissolved in pure methyl alcohol. The alcohol was then distilled off, first on a water-bath and then over a naked flame, and the resulting nearly colourless solution carefully acidified in the cold with very dilute sulphuric acid (1 : 6). In this way, the methyldehydrohexonocarboxylic acid was thrown down as a beautifully white, crystalline precipitate, which after collecting, well washing with water, and drying on a porous plate, was obtained as a colourless, crystalline powder, melting at 118—119°. This was dissolved in dilute ammonia, the solution carefully neutralised with nitric acid, and precipitated with nitrate of silver. The silver salt after washing and drying over sulphuric acid in a vacuum was mixed with an excess of ethyl iodide, dissolved in ten times its volume of pure dry ether, and boiled for four hours on a water-bath. The precipitated iodide of silver was filtered off from the ethereal solution, and washed two or three times with pure ether. The filtrate was then shaken with a little sodic carbonate solution, dried over potassic carbonate, and the ether distilled off, when an almost colourless oil remained, which on twice refractioning boiled constantly at 226·5—227° (760 mm.), and gave the following result on analysis:—

0·1663 gram substance gave 0·1238 gram H_2O, and 0·3864 gram CO_2.

	Theory.	Found.
C	63·53 per cent.	63·37 per cent.
H	8·24 „	8·27 „
O	28·33 „	28·36 „

The determination of the magnetic rotation of this preparation gave the following results:—

Sp. gr. $d^{9°}_{9°} = 1·0744$ $d^{20°}_{20°} = 1·0660$,

$d^{15°}_{15°} = 1·0696$ $d^{25°}_{25°} = 1·0626$.

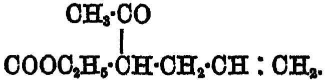
Magnetic Rotation.

t.	Sp. rotation.	Mol. rotation.
24·0	1·1314	10·060
24·0	1·1349	10·082
23·5	1·1349	10·080
23·5	1·1334	10·065
23·7	1·1336	10·069

The number 10·069 (which agrees fairly well with that obtained by the other measurements) is probably the true magnetic rotation of ethylic methyldehydrohexonecarboxylate.

Ethylic methyldehydrohexonecarboxylate does not combine with phenylhydrazine. In order to prove this, 4 grams of the pure ethereal salt were mixed with 3 grams of phenylhydrazine and gently heated on a water-bath for half-an-hour. The product, which was a comparatively limpid mass, was distilled in steam until no more oil* came over, and the distillate extracted several times with ether. The ethereal solution after drying over calcic chloride and distilling off the ether deposited 3 grams of a slightly yellowish oil, which on distilling proved to be unchanged ethylic methyldehydrohexonecarboxylate.

When the experiments on the action of trimethylene bromide on ethylic sodacetoacetate were first instituted, it was very important to show that ethylic methyldehydrohexonecarboxylate did not contain a hydrogen-atom displaceable by sodium, *i.e.*, that it was not a monosubstituted ethylic acetoacetate such as ethylic allylacetoacetate,



$$\begin{array}{l} \qquad\qquad CH_3{\cdot}CO \\ \qquad\qquad\quad | \\ COOC_2H_5{\cdot}CH{\cdot}CH_2{\cdot}CH : CH_2. \end{array}$$

This was determined by treating 10 grams of the pure ethereal salt with 1·4 grams of sodium (as sodic ethylate) and 7·5 grams of benzyl chloride. After heating on a water-bath for some hours, the product was found to consist of a mixture of benzyl ethyl ether,

$$C_6H_5{\cdot}CH_2{\cdot}O{\cdot}C_2H_5,$$

and unchanged ethylic methyldehydrohexonecarboxylate.

A few experiments were also made on the action of phosphorous pentachloride on ethylic methyldehydrohexonecarboxylate.

35 grams of the pure ethereal salt was mixed with 70 grams of chloroform and then 45 grams of phosphorous pentachloride slowly added. After each addition of the pentachloride, vigorous reaction set in, which had to be moderated by careful cooling. Towards the end the whole was warmed gently, mixed with water to decompose the phosphorous oxychloride and unchanged pentachloride, extracted with ether, and the ethereal solution washed with dilute sodic carbonate. On distilling off the ether and chloroform, a colourless oil remained behind, which after repeated fractioning under reduced pressure (200 mm.) boiled constantly at 212—215°.

Two chlorine determinations gave the following results, agreeing with the formula $C_9H_{13}O_2Cl$:—

---

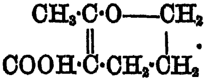
* Only traces of phenylhydrazine were carried over during the operation.

I. 0·2883 gram substance gave 0·2103 gram AgCl.
II. 0·3681 „ „ 0·2745 „

Found.	I................	18·05
	II................	18·45
Theory.	$C_9H_{13}O_3Cl$	18·83

As this substance has not been further examined, no idea can be formed as to its constitution.

Methyldehydrohexonecarboxylic Acid,



$$\begin{array}{l} CH_3\cdot C\cdot O—CH_2 \\ \qquad\;\; \| \qquad\quad | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array}.$$

This acid is easily obtained from its ethylic salt by hydrolysis with alcoholic potash. The fraction boiling between 215° and 230° is mixed with a fairly concentrated solution of alcoholic potash (containing twice the theoretical quantity of KOH) and boiled on a water-bath for six hours. The alcohol is then distilled off, the residue dissolved in a little water, gently evaporated on a water-bath to get rid of the last traces of alcohol, well cooled, and acidified with dilute sulphuric acid. In this way methyldehydrohexonecarboxylic acid is precipitated as a beautifully white, crystalline mass, which after collecting, well washing with cold water, and drying on a porous plate, is nearly pure.

To obtain the pure acid, this product is dissolved in a little boiling benzene or light petroleum (b. p. 70—90°), from which solution it crystallises on cooling in beautiful, colourless needles.

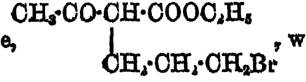
Analyses.

I. 0·1964 gram substance gave 0·1254 gram H_2O and 0·4252 gram CO_2.
II. 0·1803 gram substance gave 0·1154 gram H_2O and 0·3894 gram CO_2.
III. 0·2191 gram substance gave 0·1462 gram H_2O and 0·4768 gram CO_2.

	Theory. $C_7H_{10}O_3$.		Found.	
		I.	II.	III.
C........	59·15 per cent.	59·05	58·90	59·35
H........	7·05 „	7·09	7·11	7·41
O........	33·80 „	33·86	33·99	33·24

Methyldehydrohexonecarboxylic acid melts at 119°, but decomposes at a somewhat higher temperature into carbonic anhydride and methyldehydrohexone, as will be described later on. If, however, a small quantity of the acid is rapidly heated in a test-tube, it distils almost without decomposition, and solidifies on the cooler portions of the tube in beautiful, leaf-like crystals. It is easily soluble in hot benzene, light petroleum, alcohol, chloroform and ether, but more sparingly so in these solvents in the cold. When mixed with hot water, it dissolves readily, and the solution, if rapidly cooled, deposits the greater part of the acid in beautiful, colourless needles. On boiling with water, methyldehydrohexonecarboxylic acid is rapidly decomposed into carbonic anhydride and acetobutyl alcohol (see p. 718). In alkaline solutions this acid is very stable, and can be boiled for hours with strong potash without any apparent decomposition.

When heated at 200° with strong aqueous ammonia, it is split up into carbonic anhydride, acetobutyl alcohol, and a volatile base, which from its odour and reactions would appear to be a derivative of pyridine.

I have not further examined this base, but from its method of preparation it is probable that it is closely related to the interesting base obtained by Lipp (*Ber.*, 18, 3282) by treating ethylic ω-bromopropylacetoacetate,  $\begin{array}{l}CH_3{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5\\ \;|\\ CH_2{\cdot}CH_2{\cdot}CH_2Br\end{array}$, with alcoholic ammonia.

Methyldehydrohexonecarboxylic acid dissolves easily in concentrated aqueous solution of hydrogen bromide (sp. gr. 1·83), and if the solution be quickly extracted with ether, a brominated acid is obtained, which, however, is very unstable and cannot be obtained in a pure state; but if the acid solution be allowed to stand at ordinary temperatures, carbonic anhydride is slowly evolved, and if after some hours water be added, a heavy oil is precipitated; this, after extracting with ether, seemed to be nearly pure acetobutyl bromide, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$ (see p. 721).

When exposed to the vapour of bromine, methyldehydrohexonecarboxylic acid appears in the first case to form an unstable additive product. By the further action of the bromine, substitution takes place with evolution of hydrogen bromide. 2·036 grams of acid, after standing in an atmosphere of bromine for two days had taken up 4·767 grams of bromine = 234 per cent. calculated for the equation

$$C_7H_{10}O_3 + 4Br_2 = C_7H_6Br_4O_3 + 4HBr = 232 \text{ per cent.}$$

The product of this reaction was a thick, uninviting syrup, which could not be obtained in a crystalline form, and therefore was not analysed.

Salts of Methyldehydrohexonecarboxylic Acid.

Ammonium Salt.—To prepare this salt the pure acid is dissolved in a slight excess of ammonia, and the solution allowed to evaporate to dryness over sulphuric acid in a vacuum. It is a white, crystalline solid, very easily soluble in water.

Silver Salt, $C_7H_9O_3Ag$.—If silver nitrate is added to a neutral solution of ammonium methyldehydrohexonecarboxylate, a white, crystalline precipitate of the silver salt is thrown down. This, after collecting, well washing with water, and drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

I. 0·2997 gram substance gave 0·1010 gram H_2O, 0·3705 gram CO_2, and 0·1299 gram Ag.
II. 0·4668 gram substance gave 0·2027 gram Ag.

	Theory. $C_7H_9O_3Ag$.		Found. I.	Found. II.	
C......	33·73	per cent.	33·64	—	per cent.
H	3·62	„	3·74	—	„
Ag	43·37	„	43·24	43·41	„
O	19·27	„	19·28	—	„

This silver salt dissolves fairly easily in boiling water, and crystallises on cooling in beautiful, leafy tufts. It is very stable, and is only very slowly decomposed on boiling with water or exposing to light.

Copper Salt.—Copper methyldehydrohexonecarboxylate is precipitated on the addition of cupric sulphate to the neutral solution of the ammonium salt as a light-green, amorphous precipitate almost insoluble in water. It was collected, well washed with water, and dried over sulphuric acid in a vacuum.

Analyses.

I. 0·3337 gram substance gave 0·0720 gram CuO.
II. 0·4020 „ „ 0·0870 „

	Found. I.	Found. II.	Theory. $(C_7H_9O_3)_2Cu + H_2O$.
Cu	17·22	17·28 p. c.	17·42 p. c.

This copper salt, therefore, appears to contain 1 mol. H_2O. Unfortunately this could not be determined by a direct experiment, as the salt when heated begins to decompose at 90—100°.

Action of Water on Methyldehydrohexonecarboxylic Acid. Formation of Acetobutyl Alcohol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

When recrystallising methyl dehydrohexonecarboxylic acid from hot water, it was noticed that if the boiling was carried on for any length of time carbonic anhydride was evolved, and on cooling no crystals separated out. As the decomposition of the acid, which evidently takes place here, might throw some light on its constitution, it was carefully studied. 20 grams of the pure acid was boiled with 70 grams of distilled water in a vessel, provided with a reversed condenser, the end of which was connected with a flask containing baryta-water. The acid slowly dissolved with evolution of a considerable quantity of gas, which on passing through the baryta-water instantly caused the precipitation of baric carbonate. After boiling for about half an hour no more gas was given off, and the reaction was complete. The solution now contains acetobutyl alcohol, which is extracted in the following way.

The colourless liquid, after filtering, is treated with anhydrous potassic carbonate until thoroughly saturated, and allowed to stand for a short time, the greater part of the acetobutyl alcohol has then separated as a thick oily layer on the surface of the liquid. This is extracted ten times with ether, the ethereal solution dried over potassic carbonate, filtered, and the ether distilled off. The residue, which consists of almost pure acetobutyl alcohol, on rapid distillation passes over between 226—227°, almost without decomposition. On analysis the following results were obtained:—

I. 0·1974 gram substance gave 0·1834 gram H_2O and 0·4497 gram CO_2.

II. 0·1711 gram substance gave 0·1480 gram H_2O and 0·4042 gram CO_2.

Theory.		Found.	
$CH_3\cdot CO\cdot CH_2\,CH_2\cdot CH_2\cdot CH_2\,OH$.		I.	II.
C	62·07 per cent.	62·12	62·21 per cent.
H	10·34 "	10·33	10·09 "
O	27·59 "	27·55	27·70 "

Acetobutyl alcohol is a thick, colourless oil, which distils at 220—227° (760 mm.), with the formation of traces of an anhydride, probably methyldehydrohexone. It mixes with water in all proportions, forming a solution of burning but slightly sweet taste. It does not reduce Fehling's solution, or an ammoniacal solution of silver oxide in the cold. On warming with these reagents, a very slow reduction takes place in the case of the Fehling's solution, but the silver solution is, on the contrary, very quickly reduced, a bright mirror being formed on the sides of the vessel containing it.

Phenylhydrazine hydrochloride, dissolved in a solution of sodic acetate, produces at first a turbidity only on the addition to an aqueous solution of acetobutyl alcohol; in a short time, however, the phenylhydrazine compound separates out in large, yellow, oily drops. Several attempts were made with the object of obtaining this interesting substance in a crystalline condition suitable for analysis, but without success.

When mixed with concentrated nitric acid, acetobutyl alcohol is not attacked in the cold; on warming gently, a dark pink coloration is first formed, and on further heating oxidation rapidly sets in, torrents of red fumes being evolved.

An aqueous solution of acetobutyl alcohol, if treated with iodine and potash, gives quantities of iodoform.

Acetobutyl alcohol has been subjected to physical examination by my father, with the following results:—

Sp. gr. $d\frac{4^\circ}{4^\circ} = 0·99771,$

$d\frac{15^\circ}{15^\circ} = 0·98947,$

$d\frac{25^\circ}{25^\circ} = 0·98270.$

Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
19·5	0·99101	6·402
19·5	0·9972	6·515
17·5	0·9969	6·504
17·5	0·9960	6·498
18·5	0·9953	6·502

From its method of preparation, and the numbers obtained as its magnetic rotation, there can scarcely be a doubt that the acetobutyl alcohol described above really has the constitution assigned to it, but as it was most important in explaining the constitution of these methyldehydrohexone-derivatives to be perfectly certain on this point, it was thought that some additional evidence of its constitution was necessary.

If acetobutyl alcohol were oxidised with chromic acid, the first product which should result would be acetobutyric acid, thus:—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + O_2 = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + H_2O,$$

and on further oxidation with an excess of the oxidising agent, acetic and succinic acids should be formed, according to Popoff's rule (*Annalen*, **161**, 285)—

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + 5O = CH_3\cdot COOH + COOH\cdot CH_2\cdot CH_2\cdot COOH + H_2O.$$

Acetobutyric acid has been prepared by Wolff (*Annalen*, **216**, 129), who describes it as a thick, oily liquid, boiling at 274—275°.

On oxidising acetobutyl alcohol with the calculated quantity of chromic acid and sulphuric acid, I obtained an oily acid which possessed all the properties of acetobutyric acid. As, however, without working with large quantities of acetobutyl alcohol it would have been difficult to prove definitely the identity of the two acids, it was thought more satisfactory to examine the end products of the oxidation of this alcohol. To this purpose 4 grams of pure acetobutyl alcohol was dissolved in 20 grams of water, and then slowly mixed with a slight excess of a solution of potassic dichromate in dilute sulphuric acid. As soon as the oxidation, which set in at once, was complete, the product was submitted to distillation in steam until the condensed water showed neutral reaction. The distillate was then digested with a slight excess of baric carbonate, filtered, and the filtrate evaporated to dryness, when a considerable quantity of a white residue remained. On the addition of silver nitrate to a clear solution of this salt in water, a beautiful, crystalline salt was thrown down, which possessed all the properties of acetate of silver. It was filtered off, washed with water, dried over sulphuric acid in a vacuum, and analysed, with the following result:—

0·4657 gram substance gave 0·3010 gram Ag.

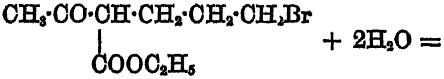
	Theory. $CH_3\cdot COOAg$.	Found.
Ag	64·66	64·64 per cent.

Acetic acid was therefore one of the products of the oxidation of acetobutyl alcohol.

The residue remaining in the retort, after distilling off the acetic acid, was made slightly alkaline by the addition of caustic potash, well boiled until all the chromium had been precipitated, the precipitate filtered off and washed. The filtrate was then rendered slightly acid with dilute sulphuric acid, evaporated to dryness on a water-bath, and the finely powdered residue extracted several times with hot alcohol. The alcoholic solution was evaporated, the dry residue again extracted with alcohol and evaporated, when a white, crystalline substance was obtained, showing all the properties of succinic acid. After once recrystallising from water, colourless crystals were obtained, melting at 180—182°,(succinic acid 180°). The solution in water gave, on the addition of ferric chloride, the characteristic, brown-red precipitate. In order to prove that this acid really was succinic acid, it was heated in a small retort for some time to its boiling point, and then distilled. After reheating and redistilling, a colourless mass of succinic anhydride was obtained, melting at 118—119°. This was further characterised by conversion into succinylfluoresceïn by heating with resorcinol.

The end products of the oxidation of acetobutyl alcohol are therefore acetic acid and succinic acid, a proof that this substance has the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

Under the name acetobutyl alcohol, a substance has already been described by Lipp (*Ber.*, 18, 3280), who prepared it by boiling ethylic ω-bromopropylacetoacetate with dilute hydrochloric acid—



$$\underset{\textstyle COOC_2H_5}{CH_3{\cdot}CO{\cdot}CH}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + 2H_2O =$$
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + HBr + C_2H_5{\cdot}OH + CO_2.$$

Lipp describes it as a fairly mobile oil, smelling of camphor and boiling at 154—155° (718 mm.), whereas the acetobutyl alcohol obtained by me was a thick, almost odourless oil, boiling at 226—227°, or as much as 70° higher than Lipp's substance.

As acetobutyl alcohol undoubtedly should be formed by the reaction used by Lipp, it is probable that he has made some slip in describing this substance. This is the more likely from the fact that the reduction product of this alcohol, hexylene glycol,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

as prepared by Lipp, has approximately the same boiling point as that obtained by me from my acetobutyl alcohol.

In order to render more complete these experiments on the decomposition of methyldehydrohexonecarboxylic acid, by boiling with water, some quantitative determinations of the amount of carbonic anhydride produced during the reaction have been made. A weighed quantity of pure acid was boiled with water in a Würtz flask connected with a reflux condenser, and the carbonic anhydride evolved, after passing through a drying-bottle containing sulphuric acid, collected in a Geissler's potash-bulb. At the end of the operation the carbonic anhydride still left in the apparatus was swept out by means of a current of air, free from carbonic anhydride, and the potash-bulbs, after standing for some time, weighed. Two experiments were made with the following results:—

I. 3·1042 grams substance gave 0·9441 gram CO_2.
II. 2·7940 „ „ 0·8500 „

	Theory.	Found. I.	Found. II.
CO_2........	30·98	30·44	30·43 per cent.

The amount of acetobutyl alcohol formed, as determined by saturating with carbonate of potash and repeatedly extracting with ether, was found in the two experiments to be about 4·2 grams, whereas the calculated amount is 4·81 grams.

It is therefore seen that the decomposition of the acid into acetobutyl alcohol and carbonic anhydride on boiling with water is a quantitative one.

δ-Hexyleneglycol, $CH_3·CH(OH)·CH_2·CH_2·CH_2·CH_2·OH$.

δ-Hexyleneglycol was first prepared by Lipp (*Ber.*, 18, 3282), who obtained it by reducing his acetobutyl alcohol with sodium amalgam. As this substance, and more especially its dibromide, were of great value for the further development of these researches on the synthetical formation of closed carbon-chains, I have repeated Lipp's experiments with my acetobutyl alcohol. 10 grams of the pure alcohol were dissolved in a little water and treated with 50 grams of 3 per cent. sodium amalgam, as described by Lipp. As soon as the reduction was finished, the product was saturated with carbonic anhydride, and extracted several times with ether. After drying over potassic carbonate and distilling off the ether, a thick oil remained, which on twice refractioning boiled fairly constantly at 228—233°, and gave the following results on analysis:—

0·1527 gram substance gave 0·1649 gram H_2O and 0·3411 gram CO_2.

	Theory. $C_6H_{14}O_2$.	Found.
C	61·01 per cent.	60·92 per cent.
H......	11·86 „	11·98 „
O......	27·13 „	27·10 „

This substance agrees in all its properties with the δ-hexyleneglycol described by Lipp.

δ-Hexylene Dibromide, $CH_3·CHBr·CH_2·CH_2·CH_2·CH_2Br$.

This substance is easily prepared in the following way:—Pure δ-hexyleneglycol is dissolved in an excess of fuming hydrobromic acid, and the mixture heated in a sealed tube at 120° for two hours. The contents of the tube are then cooled to 0°, resaturated with hydrogen bromide, and again heated in a sealed tube as before at 120° for two hours. The product, which consists of two layers, is extracted with ether, dried over calcic chloride, and rapidly fractioned under 100 mm. pressure. It is then easily obtained pure, boiling at 153—154° (100 mm.).

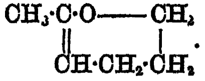
Analysis.

0·2390 gram substance gave 0·3654 gram AgBr.

	Theory. $C_6H_{12}Br_2$.	Found.
Br......	65 58 per cent.	65 34 per cent.

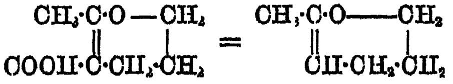
δ-Hexylene bromide is a heavy, colourless liquid, which, on standing for any length of time, undergoes slight decomposition, at the same time turning slightly dark-coloured. A detailed description of this interesting substance is reserved for a future paper.

Methyldehydrohexone,



$$\begin{array}{l} CH_3\cdot C\cdot O — CH_2 \\ \quad \| \qquad\qquad | \\ \quad CH\cdot CH_2\cdot CH_2 \end{array}.$$

If pure methyldehydrohexonecarboxylic acid is gently heated in a small retort to a temperature of 140—150° decomposition sets in,[*] carbonic anhydride is evolved, and a colourless oil distils over which consists of nearly pure methyldehydrohexone. This reaction takes place according to the following equation:—



$$\begin{array}{l} CH_3\cdot C\cdot O — CH_2 \\ \qquad\quad \| \qquad | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} = \begin{array}{l} CH_3\cdot C\cdot O — CH_2 \\ \quad \| \qquad\qquad | \\ \quad CH\cdot CH_2\cdot CH_2 \end{array}$$

As a considerable quantity of methyldehydrohexone was required for physical measurements and other experiments, as much as 30 grams of the pure acid were operated on. This amount on slow distillation gave 19 8 grams of oil (theory 20·7 grams), which on carefully fractioning nearly all passed over between 109—110° as a colourless, limpid liquid, which on analysis gave the following results:—

I. 0·2246 gram substance gave 0 2091 gram H_2O and 0·6015 gram CO_2.

II. 0·1557 gram substance gave 0·1466 gram H_2O and 0·4186 gram CO_2.

III. 0·1731 gram substance gave 0 1594 gram H_2O and 0·4640 gram CO_2.

---

[*] This acid begins to give off carbonic anhydride at 128—130°, the decomposition being very rapid at 145—150°.

	Theory. $C_6H_{10}O$.	Found I.	Found II.	Found III.
C	73·47 p. c.	73·04	73·32	73·10 p. c.
H	10·20 „	10·34	10·46	10·23 „
O	16·33 „	16·62	16·22	16·67 „

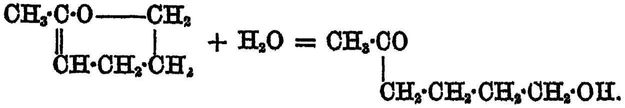
Methyldehydrohexone is a colourless, mobile, ethereal-smelling liquid which boils constantly at 109—109·5°. In preparing it, it is very important to start from pure acid. If crude methyldehydrohexonecarboxylic acid is used, peculiar condensation-products of high boiling point are formed in large quantity; they have not been further examined. Their formation appears to be due to the presence of a trace of sulphuric acid, which is difficult to completely wash out of the crude acid.

Methyldehydrohexone being the anhydride of acetobutyl alcohol, a careful study of its behaviour towards water seemed interesting. 5 c.c. of the pure substance when shaken with an equal volume of water did not appear to dissolve at all, but on standing for 24 hours the volume of the upper layer (that is of the methyldehydrohexone) had diminished to 3·6 c.c. and in another 24 hours to 2·4 c.c. After standing for about four days, the upper layer had entirely disappeared, a clear solution being formed. This on saturation with potassic carbonate deposited a quantity of a colourless oil, which on extracting with ether, drying over potassic carbonate, and fractioning, boiled almost constantly at 226—228°, and was evidently pure acetobutyl alcohol. The analysis gave the following results:—

0·1317 gram substance gave 0·1233 gram H_2O and 0·3004 gram CO_2.

	Theory. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.	Found.
C	62·07 per cent.	62·20 per cent.
H	10·34 „	10·40 „
O	27·59 „	27·40 „

The formation of acetobutyl alcohol from methyldehydrohexone by the action of water takes place according to the following equation:—



This transformation takes place much more rapidly when methyldehydrohexone is warmed with water, and is then usually finished in a few hours.

The magnetic rotation of methyldehydrohexone has been determined by my father with the following results:—

Specimen I, b. p. 109—109·5°.

Sp. gr.

$$d\frac{4^\circ}{4^\circ} = 0{\cdot}92272,$$

$$d\frac{15^\circ}{15^\circ} = 0\ 91278,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}90502.$$

t.	Sp. rotation.	Mol. rotation.
17·5	1·0123	6·051
17·5	1·0156	6·071
18·0	1·0126	6·056
18·0	1·0121	6·052
17·7	1·0131	6·057

This specimen was then carefully refractioned and found to boil at the same temperature. It was again remeasured with the following results:—

$$d\frac{15^\circ}{15^\circ} = 0{\cdot}91225.$$

t.	Sp. rotation.	Mol. rotation.
22·5	1·0115	6·072
22·5	1·0130	6·076
22·5	1·0122	6·074

Action of Hydrogen Bromide on Ethylic Methyldehydrohexonecarboxylate.

Formation of Acetobutyl Bromide, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.

Ethylic methyldehydrohexonecarboxylate dissolves readily in a strong solution of hydrogen bromide, producing a colourless liquid which, however, on standing soon turns brown, with evolution of carbonic anhydride. In studying the product of this reaction, the pure ethereal salt was mixed with two or three times its volume of hydrobromic acid (sp. gr. 1·83), and then allowed to stand until the evolution of carbonic anhydride had ceased, which was the case after about two days. On the addition of water, the dark, brownish-coloured product deposited a heavy oil which was taken up in ether and well washed first with water and then with a dilute solution of sodic carbonate. After drying over calcic chloride and distilling off the ether, the residue was purified by rapid distillation. In this way a colourless oil was obtained which boiled constantly at 214—215°, and gave the following numbers on analysis:—

I. 0·1453 gram substance gave 0·1509 gram AgBr.
II. 0·2498 „ „ 0·2538 „

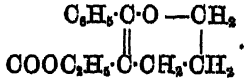
	Theory. $C_6H_{11}OBr$.	Found. I.	Found. II.
Br	44·69 p. c.	44·22	43·20 p. c.

Acetobutyl bromide is a colourless oil having a penetrating and disagreeable camphor-like odour. On standing in the air it gives off a small quantity of hydrogen bromide and gradually becomes darkly coloured. When boiled with water or dilute hydrochloric acid it seems to be slowly converted into acetobutyl alcohol.

It is probably identical with the substance obtained by Lipp (*Ber.*, **18**, 3282) by distilling his acetobutyl alcohol with hydrogen bromide solution.

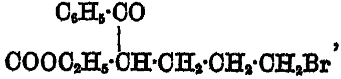
Action of Trimethylene Bromide on Ethylic Benzoylacetate.

Ethylic Phenyldehydrohexonecarboxylate,



$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}O-CH_2 \\ \qquad\;\, \| \qquad\quad | \\ COOC_2H_5{\cdot}C{\cdot}CH_2{\cdot}CH_2 \end{array}.$$

This substance, a short description of which appeared some time ago (*Ber.*, **16**, 1790), is prepared in the following way:—A solution of 2·5 grams of sodium in 30 grams of absolute alcohol, after well cooling, is mixed with 20 grams of pure ethylic benzoylacetate and then heated to gentle boiling on a water-bath with 21 grams of trimethylene bromide. The reaction sets in almost immediately, and is usually finished in two or three hours, as is shown by the liquid becoming perfectly neutral to test-paper. At this stage of the decomposition a substance containing bromine, probably ethylic ω-bromopropylbenzoylacetate,



$$\begin{array}{l} \qquad\qquad C_6H_5{\cdot}CO \\ \qquad\qquad | \\ COOC_2H_5{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br \end{array},$$

is present, which by the further action of sodic ethylate is transformed into ethylic phenyldehydrohexonecarboxylate. To effect this transformation, the product is well cooled, mixed with a second quantity of sodic ethylate (containing, as before, 2·5 grams of sodium), and heated again on a water-bath until the product, on testing, shows neutral reaction. This is usually the case in about five or six hours. The brownish-coloured mass, after cooling, is filtered from the precipitated sodium bromide, the precipitate well washed with absolute alcohol, and the filtrate distilled on a water-bath until nearly all the alcohol has been removed. The residue is then mixed with water, and the oil which separates extracted two or three times with ether. The ethereal solution after washing, drying over calcic chloride, and evaporating, leaves a dark-coloured oil behind which, after standing for some days over sulphuric acid in a vacuum, deposits a quantity of long crystals. These are separated from the mother-liquor by filtering with the aid of a vacuum pump and washing with small quantities of ether. The resulting almost colourless mass is dissolved in as small a quantity of warm ether as possible, and the solution allowed to evaporate slowly at the ordinary temperature, when the new substance separates in long, colourless prisms which, after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

I. 0·1866 gram substance gave 0·4929 gram CO_2 and 0·1197 gram H_2O.

II. 0·1973 gram substance gave 0·5214 gram CO_2 and 0·1240 gram H_2O.

	Theory. $C_{14}H_{16}O_3$.	Found. I.	Found. II.
C	72·41 p. c.	72·04	72·07 p. c.
H	6·89 „	7·13	6·98 „
O	20·69 „	20·83	20·95 „

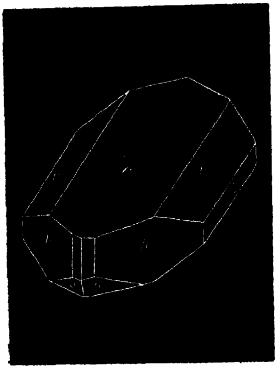
Ethylic phenyldehydrohexonecarboxylate melts at 59—60° and distils at a high temperature almost without decomposition. It is readily soluble in most of the usual solvents, and can be obtained by the slow evaporation of its solutions in ether, bisulphide of carbon, and light petroleum in magnificent, colourless, prisms. Professor Haushofer was kind enough to measure some crystals which were grown in a saturated ethereal solution of the substance. He gave me the following description of the results of his experiments:—

Ethylic Phenyldehydrohexonecarboxylate.

Crystalline system. Monoclinic.

$a : b : c = 1{\cdot}0017 : 1 : 0{\cdot}5914.$

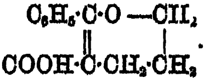
$\beta = 68° 34'.$



Moderately large but incompletely developed crystals of the combination 0P (*c*) , ∞P (*p*) , Ꝑ∞ (*r*) , ∞Ꝑ∞ (*b*) , Ꝑ½ (*o*) , ∞Ꝑ½ (*s*) The faces *s* and *o* are generally very small; *c* and *r* generally run into one another, the angle between them becoming rounded.

	Measured		Calculated.		
$c : p =$	*105°	30′	—	—	
$p : p =$	*94	0	—	—	front
$c : r =$	*151	10	—	—	
$r : r =$	122	30	122°	20′	top
$r : r =$	57	46	57	40	side
$s : s =$	130	0	130	0	
$o : o =$	132	1	132	4	
$r : p =$	124	13	124	16	

Phenyldehydrohexonecarboxylic Acid,



$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}O - CH_2 \\ \quad\quad\;\; \| \quad\quad\;\; | \\ COOH{\cdot}C{\cdot}CH_2{\cdot}CH_2 \end{array}.$$

To obtain this acid, 5 grams of ethylic phenyldehydrohexonecarboxylate is boiled with a fairly concentrated solution of alcoholic potash (containing 2 grams of KOH) for about four hours on a water-bath After distilling off the alcohol, a little water is added, the almost colourless solution gently evaporated until the last trace of alcohol has been driven off, and then filtered. On acidifying the filtrate with dilute sulphuric acid, the new acid is precipitated as a white, crystalline mass. This is collected, well washed with water, dried on a porous plate, and recrystallised from ether. It is thus obtained in beautiful, colourless prisms which, after drying over sulphuric acid in a vacuum, gave the following numbers :—

0·1914 gram substance gave 0·4930 gram CO_2 and 0·1041 gram H_2O.

	Theory. $C_{12}H_{12}O_2$.	Found.
C	70·59 per cent.	70·25 per cent.
H	5·88 „	6·04 „
O	23·53 „	23·71 „

Phenyldehydrohexonecarboxylic acid melts at about 142—144° with evolution of carbonic anhydride. It is easily soluble in alcohol, chloroform, benzene, carbon bisulphide, ether, and light petroleum almost insoluble in cold water. When in a very finely-divided state it dissolves, however, to a considerable extent in boiling water, and crystallises out again on cooling in fine, colourless needles. The most beautiful crystals are obtained when a concentrated ethereal solution of the acid is allowed to evaporate at ordinary temperatures.

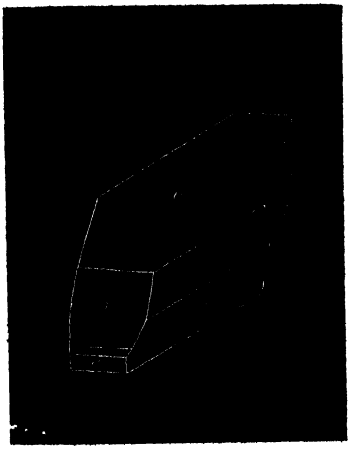
Professor Haushofer, who was kind enough to examine some of these, gave the following description of them :—

Phenyldehydrohexonecarboxylic Acid.

Crystalline System. Monoclinic.

$a : b : c = 2·6379 : 1 : 3·3984.$

$\beta = 74° 44'.$



Beautifully lustrous, well-developed crystals of the combination $0P\ (c),\ -P\ (w),\ P\ (o),\ -\bar{P}\infty\ (r)\ -2\bar{P}\infty\ (s)\ \infty\bar{P}\infty\ (a)$. In many crystals the face *s* is missing, whilst on others it completely disappears into *a*; neither of these faces admit of accurate measurement as they are, as a rule, flawed and rounded; *c* also shows many flaws.

	Measured.		Calculated.	
w =	*110°	54′		
o =	*100	40		
o =	*46	28		
w =	58	10	58°	16′
r =	137	1	137	8
r =	119	5	119	8
a =	148	15	148	8
a =	105 approx.		105	16
w =	138	40	138	50
o =	148	27	148	26
a =	106	50	106	44
c : *s* =	124 approx.		124	2

The plane of the optical axis is the plane of symmetry, $\infty\grave{P}\infty$. The polarisation figure of one axis is visible on the face *c* (in the obtuse angle β).

Salts of Phenyldehydrohexonecarboxylic Acid.

Phenyldehydrohexonecarboxylic acid dissolves easily in alkalis, alkaline carbonates, and ammonia. Its solution in a slight excess of ammonia was allowed to stand for some hours over sulphuric acid in a vacuum until quite neutral, and then the following salts prepared by precipitation with various reagents.

The *silver salt* is thrown down on the addition of nitrate of silver as a white, crystalline precipitate which, after collecting, well washing with water, and drying over sulphuric acid in a vacuum, was analysed with the following result:—

0·2735 gram substance gave 0·0952 gram silver.

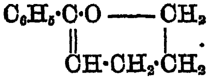
	Theory. $C_{13}H_{11}O_3Ag$.	Found.
Ag......	34·73 per cent.	34·81 per cent.

This silver salt dissolves, though not easily, in boiling water, and separates out again on cooling in beautiful, colourless needles.

The *copper salt* is obtained as a light-green precipitate on adding a solution of cupric sulphate to the ammonium salt.

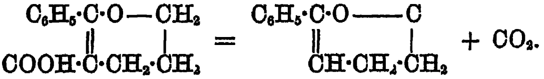
The *lead salt* is a white precipitate insoluble in water; *calcic* and *baric* chlorides give no precipitate when added to a solution of the ammonium salt.

Phenyldehydrohexone,



$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}O\text{——}CH_2 \\ \ \ \Vert \qquad\quad\ \ \vert \\ CH{\cdot}CH_2{\cdot}CH_2 \end{array}.$$

When phenyldehydrohexonecarboxylic acid is heated a few degrees above its melting point, rapid decomposition into carbonic anhydride and phenyldehydrohexone takes place thus:—



$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}O\text{—}CH_2 \\ \qquad\ \Vert \qquad\ \vert \\ COOH{\cdot}C{\cdot}CH_2{\cdot}CH_2 \end{array} = \begin{array}{l} C_6H_5{\cdot}C{\cdot}O\text{——}C \\ \ \ \Vert \qquad\quad\ \ \vert \\ CH{\cdot}CH_2{\cdot}CH_2 \end{array} + CO_2.$$

In order to examine the products of this reaction, the pure acid was heated in a small Wurtz flask in a metal bath at about 200° until the evolution of carbonic anhydride had ceased, and the resulting oil fractioned. On the first distillation, the whole passed over between 235—255°, and on refractioning once or twice the pure substance was obtained as a colourless oil boiling constantly at 249—251° (720 mm.).

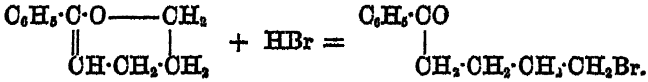
Analyses.

I. 0·1712 gram substance gave 0·1166 gram H_2O and 0·5164 gram CO_2.

II. 0·1645 gram substance gave 0·1138 gram H_2O and 0·4952 gram CO_2.

	Theory. $C_{11}H_{12}O$.	Found. I.	Found. II.
C	82·50 p. c.	82·27	82·10 p. c.
H	7·50 „	7·56	7·69 „
O	10·00 „	10·17	10·21 „

Phenyldehydrohexone is a thick, colourless, aromatic-smelling oil, which boils almost without decomposition at 249—251°. After long standing it polymerises and becomes quite gelatinous. It does not appear to combine with phenylhydrazine. It is insoluble in cold water, but on long boiling a part seems to dissolve, probably being converted into benzoylbutyl alcohol. When dissolved in concentrated aqueous hydrogen bromide, phenyldehydrohexone is converted quantitatively into benzoylbutyl bromide, thus:—



$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}O\text{——}CH_2 \\ \ \ \Vert \qquad\quad\ \ \vert \\ CH{\cdot}CH_2{\cdot}CH_2 \end{array} + HBr = \begin{array}{l} C_6H_5{\cdot}CO \\ \ \vert \\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br. \end{array}$$

Action of Hydrogen Bromide on Phenyldehydrohexonecarboxylic Acid and Phenyldehydrohexone.

Formation of Benzoylbutyl Bromide, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$.

Phenyldehydrohexonecarboxylic acid dissolves easily in concentrated aqueous hydrogen bromide (sp. gr. 1·83) with evolution of heat. If the solution be allowed to stand, much carbonic anhydride is evolved, and in about one hour the whole solidifies to a mass of crystals of benzoylbutyl bromide. These are filtered off on a vacuum-pump, washed with a small quantity of water, and dried on a porous tile over sulphuric acid in a vacuum. They are then further purified by recrystallisation from petroleum ether (b. p. 45—70°).

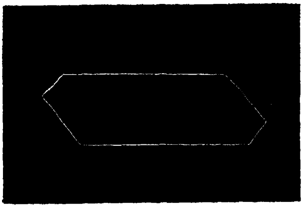
Analyses.

I. 0·1683 gram substance gave 0·0828 gram H_2O, and 0·3360 gram CO_2.

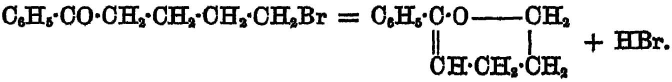
II. 0·2928 gram substance gave 0·2288 gram AgBr.

	Theory. $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$.	Found. I.	Found. II.	
C	54·77 p. c.	54·45	—	p. c.
H	5·39 „	5·47	—	„
Br	33·19 „	—	33·25	„
O	6·64 „	—	—	„

Benzoylbutyl bromide melts at 61°. It is easily soluble in alcohol, benzene, chloroform, carbon bisulphide, ether, and light petroleum, almost insoluble in water. It crystallises from dilute alcohol in glistening plates, which have very much the appearance of benzoic acid. From light petroleum it crystallises in six-sided plates, which have the form



When warmed with alcoholic potash benzoylbutyl bromide is transformed into phenyldehydrohexone.

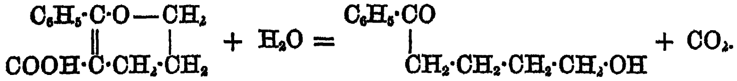


$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br = \begin{array}{l} C_6H_5\cdot C\cdot O\text{——}CH_2 \\ \qquad\ \| \qquad\quad | \\ \qquad\ CH\cdot CH_2\cdot CH_2 \end{array} + HBr.$$

Benzoylbutyl bromide is most easily prepared from phenyldehydrohexone. If this substance is dissolved in twice its volume of highly concentrated aqueous hydrogen bromide and then cooled, the whole solidifies to a mass of crystals of benzoylbutyl bromide, which when treated as described above are easily obtained pure.

Action of Water on Phenyldehydrohexonecarboxylic Acid.

When boiled with water for any length of time, phenyldehydrohexonecarboxylic acid is split up into benzoylbutyl alcohol and water, thus:—



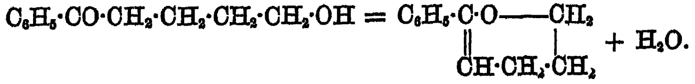
$$\begin{array}{l} C_6H_5\cdot C\cdot O - CH_2 \\ \qquad \Vert \qquad\ | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} + H_2O = \begin{array}{l} C_6H_5\cdot CO \\ | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH \end{array} + CO_2.$$

It is necessary to have the acid in as finely divided a state as possible, in order that it may dissolve in the water, and this is easily brought about by dissolving it in dilute ammonia and then carefully reprecipitating with dilute sulphuric acid. The fine powder thus obtained is collected, washed with water, and well agitated with boiling water until it completely dissolves. On boiling this solution in a reflux apparatus decomposition sets in, and carbonic anhydride is rapidly evolved, the reaction being generally finished in about six or eight hours. The resulting clear solution on the addition of anhydrous potassic carbonate, yields the benzoylbutyl alcohol in oily drops; it is extracted four or five times with ether, and dried over potassic carbonate. On evaporating this ethereal solution, a colourless oil is obtained which in a short time solidifies to a crystalline cake. This, after drying rapidly on a porous plate over sulphuric acid in a vacuum, was analysed with the following result:—

0·1134 gram substance gave 0·3010 gram CO_2 and 0·0798 gram H_2O.

	Theory. $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C	74·27 per cent.	74·51 per cent.
H	7·86 „	7·80 „
O	17·97 „	17·69 „

If this alcohol is left for a few hours over sulphuric acid in a vacuum, the crystals gradually disappear and give place to a colourless oil. The small quantity of crystals at my disposal had thus in four days completely liquefied, and therefore I was not able to take a melting point or examine the properties. I hope, however, to be able to fill up those details at a later date. The change which takes place here is simply elimination of water and formation of the anhydride, phenyldehydrohexone, thus:—



$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH = \begin{array}{l} C_6H_5\cdot C\cdot O\text{——}CH_2 \\ \qquad\ \ \| \qquad\quad\ \ | \\ \qquad\ CH\cdot CH_2\cdot CH_2 \end{array} + H_2O.$$

An analysis of the substance obtained after the benzoylbutyl alcohol had stood over sulphuric acid for seven days, gave the following numbers:—

0·1574 gram substance gave 0·1071 gram H_2O and 0·4701 gram CO_2.

	Theory. $C_{11}H_{12}O$.	Found.
C	82·50 per cent.	82·07 per cent.
H	7·50 "	7·56 "
O	10·00 "	10·37 "

This substance is identical with the phenyldehydrohexone obtained by the dry distillation of phenyldehydrohexonecarboxylic acid, as described previously (p. 731). When dissolved in concentrated aqueous hydrogen bromide it combines with it to form benzoylbutyl bromide, which from its melting point and other properties was found to be identical with that obtained previously (p. 732).

It is curious that acetobutyl alcohol and benzoylbutyl alcohol should differ so remarkably in stability, the former even on distillation being only to a very slight extent converted into its anhydride, whereas the latter suffers this change completely at the ordinary temperature.

On the Action of Trimethylene Bromide on the Sodium-derivative of Ethylic Paranitrobenzoylacetate.

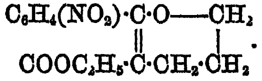
If the sodium compound of ethylic paranitrobenzoylacetate is treated with trimethylene bromide, the paranitro-derivative of ethylic phenyldehydrohexonecarboxylate is formed, the reaction taking place in a way precisely similar to that which has already been described in the last section. The only difference being that ethylic paranitrobenzoylacetate is substituted for ethylic benzoylacetate.

As ethylic paranitrobenzoylacetate, and more especially its sodium-derivative (Trans., 1886, 440), are such beautifully crystalline substances, it seemed that in this case it would be more easy to follow the mechanism of the reaction with trimethylene bromide; this was found to be the case.

Before describing these experiments I should like to thank Dr.

Gustav Bellenot for the valuable help he rendered me in carrying them out.

Ethylic Paranitrophenyldehydrohexonecarboxylate,



$$\begin{array}{l} C_6H_4(NO_2)\cdot C\cdot O\text{——}CH_2 \\ \qquad\qquad\quad \| \qquad\quad | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2 \end{array} .$$

In order to obtain this compound 10 grams of the pure sodium compound of ethylic paranitrobenzoylacetate (*ibid.*, 448), 8 grams of trimethylene bromide, and 30 grams of absolute alcohol were heated at 100° in a sealed tube for three or four hours, after which time a quantity of sodium bromide had separated out and the mixture had become neutral. 0·9 gram of sodium dissolved in the least possible quantity of absolute alcohol was then added, the tube resealed, and once more heated at 100° for four hours. The tube was then opened, and the alcohol distilled off. On adding water to the remainder, the product of the reaction separates as a thick, brownish oil, which was extracted several times with ether. After drying over calcic chloride and distilling off the ether, a dark-brown liquid remains behind, the greater part of which solidifies on standing over sulphuric acid in a vacuum. The crystals were spread on a porous plate in order to free them roughly from mother-liquor, and afterwards dissolved in a little warm ether. An equal volume of light petroleum was then added and the mixture allowed to evaporate slowly at ordinary temperatures. Magnificent, lustrous, yellow crystals were thus obtained which on analysis gave the following results :—

I. 0·2664 gram substance gave 0·1300 gram H_2O and 0·5889 gram CO_2.

I*a*. 0·1703 gram substance gave 8·2 c.c. N. $t = 15°$; bar. = 720 mm.

	Theory. $C_{14}H_{15}NO_5$.		Found.	
C......	60·64	per cent.	60·29	per cent.
H......	5·41	„	5·42	„
N......	5·05	„	5·24	„
O......	28·90	„	29·05	„

Ethylic paranitrophenyldehydrohexonecarboxylate melts at 62—63°. It is easily soluble in ether, benzene, and alcohol, sparingly so in light petroleum, insoluble in water.

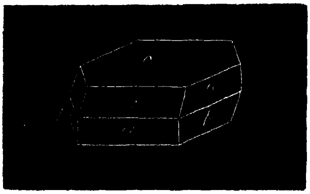
Professor Haushofer has kindly examined this beautiful substance crystallographically, and given me the following account of his experiments :—

Ethylic Paranitrophenyldehydrohexonecarboxylate.

Crystalline system. Monoclinic.

$a : b : c = 2{\cdot}3530 : 1 : 1{\cdot}8530.$

$\beta = 80° 42'.$



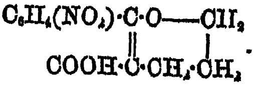
Small tabular crystals of the combination,

$0P = (001) = c$
$\infty P = (110) = p$
$\infty\bar{P}\infty = (100) = a$
$-\bar{P}\infty = (101) = r$
$-P = (111) = o$

Generally the basal plane predominates, elongated in the direction of the axis *b*. The face *c* is usually flawed or slightly curved. The faces *o* and *p* are incompletely developed. The plane of the optical axis is the plane of symmetry; one axis is approximately normal to the face *c*.

	Measured.		Calculated.	
$p : c = (110)(001)$	*93°	40′	—	—
$a : p = (100)(110)$	*113	18	—	—
$p : p = (110)(1\bar{1}0)$	—	—	46°	36′
$c : o = (001)(111)$	*119	34	—	—
$c : a = (001)(100)$	99	17	99	18
$c : r = (001)(101)$	145	21	145	25
$r : o = (101)(111)$	126	36	126	50

Paranitrophenyldehydrohexonecarboxylic Acid,



$$\begin{array}{l} C_6H_4(NO_2){\cdot}C{\cdot}O\text{——}CH_2 \\ \qquad\qquad\quad \| \qquad\quad | \\ COOH{\cdot}C{\cdot}CH_2{\cdot}CH_2 \end{array}.$$

To prepare this acid, the pure ethylic salt was mixed with a tolerably concentrated solution of alcoholic potash and allowed to stand for several hours, by which means it is easily and completely hydrolysed. Sufficient water to effect solution is added to this potassic salt, the whole, if necessary, filtered, and the filtrate acidified with dilute sulphuric acid, when the new acid is precipitated in the form of yellow flakes, which are best extracted with ether. After drying over calcic chloride and filtering, the ether is evaporated, the crude acid thus being left behind as a yellow crust, which after several times recrystallising from benzene is obtained in the form of thick, colourless needles. These on analysis gave numbers which agree well with the formula $C_{12}H_{11}NO_5$.

0·2265 gram substance gave 0·0869 gram H_2O and 0·4788 gram CO_2.

0·2467 gram substance gave 13·5 c.c. N. $t = 12°$; bar. = 718 mm.

	Theory.		Found.	
C	57·83	per cent.	57·64	per cent.
H	4·41	„	4·26	„
N	5·62	„	5·61	„
O	32·14	„	32·49	„

Paranitrophenyldehydrohexonecarboxylic acid when crystallised from benzene melts at 172°. It is easily soluble in benzene, ether, alcohol, and light petroleum, but crystallises best from benzene. The crystalline acid is almost insoluble in water. If, however, it is carefully precipitated from its solution in dilute ammonia by the addition of dilute acids, a seemingly amorphous precipitate is obtained which dissolves to a considerable extent in boiling water, and crystallises on cooling in long, colourless, glistening needles, which fuse at 183°. It will be seen that the melting point given here is 10° higher than that given for the same substance crystallised from benzene.

Phenyldehydrohexonecarboxylic acid has, as I have already shown, the same peculiarity, the thick prisms of this substance obtained from ether fusing at 142—144°, whereas the needles obtained from water melt at 149—150°.

Paranitrophenyldehydrohexonecarboxylic acid when heated above 200° is split up into carbonic anhydride and a neutral substance, which, however, has not been further examined.

The *salts* of paranitrophenyldehydrohexonecarboxylic acid are very stable. A solution of the ammonium salt is easily obtained by dissolving the free acid in a slight excess of ammonia, and then allowing the liquid to stand over sulphuric acid in a vacuum until it reacts quite neutral.

If nitrate of silver be added to this solution, a slightly yellow, amorphous *silver* salt is thrown down. This after collecting, well washing with water, and drying first in a vacuum and then at 100°, gave the following analytical results:—

0·1990 gram substance gave 0·0601 gram Ag.

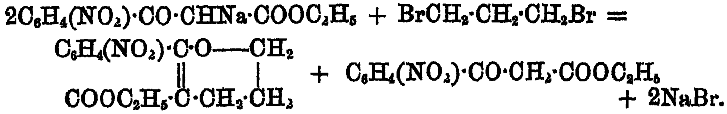
	Theory. $C_{12}H_{10}NO_5Ag$.	Found.
Ag........	30·34 per cent.	30·20 per cent.

This silver salt dissolves in hot water, and crystallises out on cooling in light yellow needles.

On adding a solution of acetate of copper to the ammonium salt, the *copper* salt is precipitated as a light-green, flocculent precipitate.

The *lead* salt is a white, amorphous precipitate almost insoluble in water.

The main object in conducting these experiments with ethylic paranitrobenzoylacetate was to prove that when the sodium-derivatives of this and analogously constituted substances are treated with dibromides such as ethylene and trimethylene bromides, the reaction really takes place between two molecules of the sodium compound and one of the bromide. Thus in the case of trimethylene bromide the reaction is:



$$2C_6H_4(NO_2)\cdot CO\cdot CHNa\cdot COOC_2H_5 + BrCH_2\cdot CH_2\cdot CH_2Br =$$

$$\begin{array}{l} C_6H_4(NO_2)\cdot C\cdot O\text{——}CH_2 \\ \qquad\quad \| \qquad\quad | \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2 \end{array} + C_6H_4(NO_2)\cdot CO\cdot CH_2\cdot COOC_2H_5 + 2NaBr.$$

The experiment was carried out in the following way:—

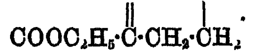
An intimate mixture of 5 grams of the pure sodium-derivative of ethylic paranitrobenzoylacetate, 4 grams of trimethylene bromide, and about 10 grams of alcohol were heated in a sealed tube at 100° until the reaction was complete (about six to eight hours). The product after gently warming on a water-bath to free it from alcohol, was treated with water and several times extracted with ether. The ethereal solution was carefully dried over calcic chloride and distilled, when a brownish-coloured, thick oil remained behind, a trace of which dissolved in alcohol and treated with ferric chloride gave a deep brownish-red coloration, showing the presence of considerable quantities of ethylic paranitrobenzoylacetate. To the solution of this oil in pure alcohol, 0·5 gram of sodium dissolved in alcohol was added. In this way, a dark-brown solution was formed, from which, on the addition of an equal volume of pure ether, a yellowish-brown sodium compound was slowly precipitated. After standing for 24 hours this was collected, washed with a mixture of ether and alcohol, and analysed with the following result:—

	Theory. $C_6H_4(NO_2)\cdot CO\cdot CHNa\cdot COOC_2H_5$.	Found.
Na......	8·88 per cent.	9·24 per cent.

This substance was therefore the sodium-derivative of ethylic paranitrobenzoylacetate. The amount obtained in this way weighed upwards of 2 grams, whereas the yield calculated for the above equation should be 2·5 grams. The filtrate from this sodium compound was now mixed with more ether, the ethereal solution well washed with water, dried over calcic chloride, and distilled, when a brownish oil was obtained, which, after long standing over sulphuric acid in a vacuum, almost entirely solidified. The crystals, after spreading on a porous plate and recrystallising from ether and light petroleum, were easily purified, and then showed all the properties of ethylic paranitrophenyldehydrohexonecarboxylate. From this result it is seen that the formation of this substance takes place according to the equation given above.

Action of Trimethylene Bromide on the Disodium-derivative of Ethylic Acetonedicarboxylate.

Ethylic Methyldehydrohexonedicarboxylate,



$$\begin{array}{l}COOC_2H_5{\cdot}CH_2{\cdot}C{\cdot}O - CH_2\\ \qquad\qquad\qquad\quad \| \qquad\ \ | \\ COOC_2H_5{\cdot}C{\cdot}CH_2{\cdot}CH_2\end{array}.$$

In studying this reaction, a mixture of 200 grams of ethylic acetonedicarboxylate and 205 grams of trimethylene bromide was slowly added to a cold solution of 46 grams of sodium dissolved in 500 grams of absolute alcohol, care being taken to cool the mass well during the mixing, as otherwise a violent reaction, difficult to control, is apt to set in. On warming the resulting clear solution on a water-bath, sodium bromide soon begins to separate out, and after boiling for 10 hours in a reflux apparatus, the reaction may be considered as being at an end. Water is now added, and the oily product of the reaction separated from the aqueous solution by extraction with ether. The ethereal solution is next evaporated, and the almost colourless oil thus obtained, submitted to distillation in a rapid current of steam until no more oil passes over with the water. In this way the product was easily separated into two nearly equal parts, each of which weighed about 90 grams. The ethylic methyldehydrohexonedicarboxylate which remains behind in the retort is extracted with ether, the ethereal solution washed with a little dilute sodic carbonate, and dried over calcic chloride. After distilling off the ether, an almost colourless oil is obtained, which is purified by fractioning under reduced pressure (150 mm.). At the first distillation nearly the whole passed over between 225—250°, leaving a small residue in the retort, and on repeatedly fractioning the distillate, an oil was at last obtained, which boiled constantly at 238—240° (150 mm.). The analysis of this fraction gave the following results:—

0·2172 gram substance gave 0·1497 gram H_2O and 0·4730 gram CO_2.

	Theory. $C_{12}H_{18}O_5$.	Found.
C......	59·50 per cent.	59·40 per cent.
H......	7·44 ,,	7·65 ,,
O......	33·06 ,,	32·95 ,,

Ethylic methyldehydrohexonedicarboxylate is a thick, colourless oil, having a disagreeable smell somewhat resembling that of ethylic methyldehydrohexonemonocarboxylate. This oil, when dissolved in alcohol gives, on the addition of a drop of ferric chloride, a beautiful violet coloration; this is, however, probably due to traces of ethylic acetonedicarboxylate, which appear always to be present in samples of ethylic methyldehydrohexonedicarboxylate prepared by the above reaction.

When mixed with alcoholic potash, a yellow solution is formed, and on heating hydrolysis rapidly sets in.

It now seemed interesting to examine the oil which distilled over with the steam during the purification of the crude product of the action of trimethylene bromide on ethylic acetonedicarboxylate, as described above. For this purpose, the aqueous distillate was extracted with ether, the ethereal solution dried over calcic chloride, filtered, the ether distilled off, and the resulting colourless oil fractioned. It was thus easily separated into two principal fractions, 170—200° and 200—235°, of which the latter was the larger. This fraction, 200—235°, yielded by repeated fractioning a beautiful, colourless oil, which boiled constantly at 223—224° (720 mm.), and on analysis proved to be ethylic methyldehydrohexonecarboxylate.

0·2081 gram substance gave 0·1572 gram H_2O and 0·4800 gram CO_2.

	Theory. $C_9H_{14}O_3$.	Found.
C........	63·53 per cent.	62·91 per cent.
H........	8·23 ,,	8·39 ,,
O........	28·23 ,,	28·70 ,,

In order to characterise this substance it was subjected to hydrolysis, and the free acid obtained recrystallised from benzene. It then melted at 119°, and showed all the properties of methyldehydrohexonecarboxylic acid. An analysis of the silver salt gave the following numbers:—

0·2805 gram substance gave 0·1209 gram of silver = 43·10 per cent.; theory $C_7H_9O_3Ag$ = 43·38 per cent.

Ethylic methyldehydrohexonecarboxylate is probably produced from the dicarboxylate by partial hydrolysis and elimination of carbonic anhydride, as described below.

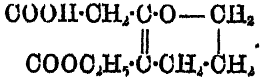
The fraction 170—200° of the original oil, on repeated distillation, was found to boil for the most part between 175—185°, and to consist of nearly pure ethylic acetoacetate. It was not thought necessary to analyse this, its reactions being so well known that identification is a matter of ease. It is evidently formed from ethylic acetonedicarboxylate by partial hydrolysis and elimination of carbonic anhydride, thus:—

$$COOC_2H_5{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 = COOH{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$$
$$= CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + CO_2.$$

a reaction which always takes place when ethylic acetonedicarboxylate is treated with alkalis.

Hydrolysis of Ethylic Methyldehydrohexonedicarboxylate.

(1.) *Hydric Ethylic Methyldehydrohexonedicarboxylate,*



$$\begin{matrix} COOH{\cdot}CH_2{\cdot}C{\cdot}O & — & CH_2 \\ \| & & | \\ COOC_2H_5{\cdot}C{\cdot}CH_2 & \cdot & CH_2 \end{matrix}.$$

The hydrolysis of ethylic methyldehydrohexonedicarboxylate takes place in two stages. In the first place an acid ethereal salt of the formula given above is formed, which then by the further action of alkalis is finally converted into the dicarboxylic acid:

$$(1.)\ C_6H_8O{<}\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} + KOH = C_6H_8O{<}\begin{matrix}COOK\\COOC_2H_5\end{matrix} + C_2H_5{\cdot}OH.$$

$$(2.)\ C_6H_8O{<}\begin{matrix}COOK\\COOC_2H_5\end{matrix} + KOH = C_6H_8O{<}\begin{matrix}COOK\\COOK\end{matrix} + C_2H_5{\cdot}OH.$$

In preparing the hydric ethylic salt, pure ethylic methyldehydrohexonedicarboxylate is mixed with a large excess of a fairly concentrated solution of alcoholic potash, and allowed to stand at the ordinary temperature, until a sample taken out dissolves completely in H_2O (10 to 14 hours). In order to isolate the new compound, dilute sulphuric acid (1 acid to 5 H_2O) is added in excess, care being taken to keep the liquid cool during the operation. The product is then extracted five or six times with ether, the ethereal solution washed until free from alcohol, dried over calcic chloride, and the ether distilled off at as low a temperature as possible. A thick oil is thus obtained, which, after standing for some days over sulphuric acid in a vacuum, almost completely solidifies to a mass of crystals. These are roughly separated from oily impurities by spreading out on a porous plate, then washed with a little pure ether, and finally completely dissolved in this solvent. If this solution is allowed to evaporate slowly at ordinary temperatures, the acid ethylic salt separates out in magnificent, colourless, transparent crystals, which after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

I. 0·2060 gram substance gave 0·1240 gram H_2O and 0·4208 gram CO_2.

II. 0·1870 gram substance gave 0·1155 gram H_2O and 0·3805 gram CO_2.

	Theory. $C_6H_8O{<}\begin{matrix}COOH\\COOC_2H_5\end{matrix}$.	Found. I.	 II.
C	56·07 per cent.	55·71	55·49
H	6·55 „	6·69	6·86
O	37·38 „	37·60	37·65

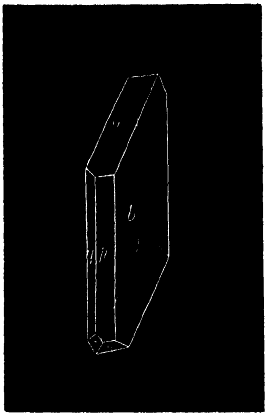
It melts at 114°, is easily soluble in alcohol and ether, and sparingly so in hot water. If the hot aqueous solution be allowed to cool slowly the substance crystallises out in beautiful, colourless, four-sided needles. The alcoholic solution gives no coloration with ferric chloride, and it is for this reason that it appeared to me likely that the beautiful coloration produced in solutions of the diethylic salt by ferric chloride was caused by the presence of traces of ethylic acetonedicarboxylate. The best solvent to crystallise the acid ethylic salt from is pure ether. In this way most magnificent crystals can be obtained. Professor Haushofer was kind enough to measure these, and gave me the following account of his experiments.

Hydric Ethylic Methyldehydrohexonedicarboxylate.

Crystalline system. Triclinic.

$a : b : c = 0·7741 : 1 : 0·3371.$

$\alpha = 89° 40'$
$\beta = 98° 18'$
$\gamma = 89° 50'$



Colourless, lustrous crystals of the combination—

$$\begin{aligned}
\infty\breve{P}\infty &= (010) = b \\
P' &= (111) = w \\
\infty P'_{|} &= (110) = p \\
P_{|} &= (11\bar{1}) = o \\
\infty{}_{|}'P &= (1\bar{1}0) = q \\
{}_{|}\breve{P}\tfrac{1}{3} &= (3\bar{1}\bar{1}) = s
\end{aligned}$$

Development tabular to the face *b*. The face *q* was only observed on a single crystal, it was very small, but sharply developed. The faces *b* are frequently rounded, and sometimes deviate some degrees from the parallel. Cleavage moderately distinct, parallel to *w*.

	Measured.		Calculated.	
$w : b = (111)(010) =$	*105°	27′	—	—
$w : p = (111)(110) =$	*123	19	—	—
$p : o = (110)(11\bar{1}) =$	*113	56	—	—
$p : q = (110)(1\bar{1}0) =$	*104	48	—	—
$p : b = (110)(010) =$	*127	19	—	—
$o : b = (11\bar{1})(010) =$	108	33	108°	37′
$q : o = (1\bar{1}0)(11\bar{1}) =$	90	20	91	3
$q : w = (1\bar{1}0)(111) =$	102	26	102	48
$s : p = (3\bar{1}\bar{1})(110) =$	117	40	117	44
$s : o = (3\bar{1}\bar{1})(11\bar{1}) =$	134	42	135	17
$: b = (3\bar{1}\bar{1})(010) =$	77	58	78	0
$s : q = (3\bar{1}\bar{1})(1\bar{1}0) =$	135	49	135	46

The results of the measurements of the angles do not absolutely exclude the possibility of the crystals belonging to the monoclinic system, whilst the smallness and brittleness of the crystals prevented the optical properties being sufficiently determined to decide the crystalline system with certainty; the direction of the only cleavage plane, however, leaves scarcely any doubt as to the crystals belonging to the triclinic system.

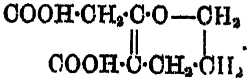
This acid ethylic salt dissolves easily in alkalis, and gives well characterised salts, of which the *silver* salt has been carefully prepared and examined. This salt is thrown down on adding nitrate of silver to a neutral solution of the ammonium salt as a white, curdy precipitate sparingly soluble in water. It was collected, well washed with water, and dried over sulphuric acid in a vacuum.

Analysis.

0·2330 gram substance gave 0·0870 gram H_2O, 0·3168 gram CO_2, and 0·0786 gram Ag.

	Theory. $C_6H_8O<\begin{matrix}COOAg\\COOC_2H_5\end{matrix}$.	Found.
C........	37·38 per cent.	37·09 per cent.
H........	4·05 ,,	4·14 ,,
Ag	33·64 ,,	33·73 ,,
O........	24·92 ,,	25·04 ,,

(2.) *Methyldehydrohexonedicarboxylic Acid,*



$$\begin{matrix}COOH\cdot CH_2\cdot C\cdot O - CH_2\\ \| \qquad\quad | \\ COOH\cdot C\cdot CH_2\cdot CH_2\end{matrix}.$$

This acid may be obtained by the hydrolysis of the acid ethylic salt, but it was usually prepared directly from ethylic methyldehydrohexonedicarboxylate. The pure ethylic salt is mixed with an excess of alcoholic potash and heated to boiling for three or four hours on a water-bath. The slightly brownish-coloured solution is then diluted with twice its volume of water, and evaporated in an open dish on a water-bath until all the alcohol has been expelled. After filtering and acidifying with dilute sulphuric acid, the solution is allowed to stand 24 hours in a cool place, at the end of which time it is usually found that a crystalline crust, consisting of the nearly pure dicarboxylic acid, has separated on the bottom of the vessel containing the liquid. This is collected, washed with a little water, and dried on a porous plate (A). The mother-liquors are then extracted four or five times with ether, the ethereal solution washed, dried over calcic chloride, and the ether distilled off. A further quantity of impure dicarboxylic acid is thus obtained, usually as a thick oil, which, however, after standing for some days over sulphuric acid in a vacuum, deposits a quantity of crystals. These are roughly separated from impurities by spreading out on a porous plate, then washed with a little ether, and mixed with the crop (A) first obtained. The whole is now dissolved in a little hot water, and the solution filtered. On standing, the dicarboxylic acid soon begins to crystallise out in colourless plates, which after collecting, washing with water, and drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

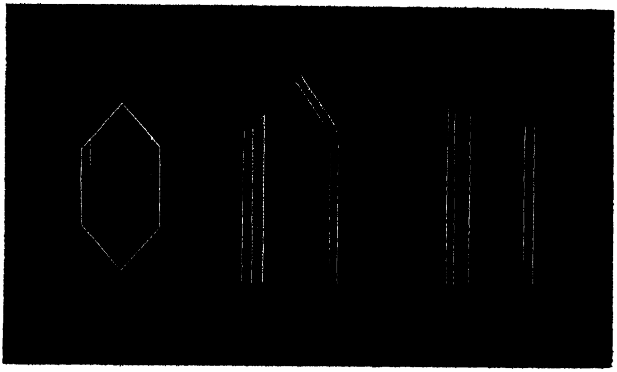
I. 0·1489 gram substance gave 0·0756 gram H_2O and 0·2819 gram CO_2.

II. 0·1757 gram substance gave 0·0889 gram H_2O and 0·3306 gram CO_2.

	Theory.	Found.	
	$C_6H_8O<\begin{matrix}COOH\\COOH\end{matrix}$.	I.	II.
C	51·61 per cent.	51·63	51·32 per cent.
H	5·38 „	5·64	5·67 „
O	43·01 „	42·73	43·01 „

Methyldehydrohexonedicarboxylic acid melts at about 185—190° with decomposition, evolution of carbonic anhydride, and formation of a curiously reddish-coloured liquid. This red coloration appears to be always produced when the pure acid is heated above its melting point, and is very characteristic. When heated in a test-tube the acid gives off carbonic anhydride, and an oil is formed which has in a marked degree the peculiar odour of methyldehydrohexone.

Methyldehydrohexonedicarboxylic acid is easily soluble in hot water and hot alcohol, but sparingly soluble in ethyl acetate, ether, and benzene. It crystallises from water in beautiful, colourless plates, which under the influence of polarised light show a fine play of colours. The forms of the crystals are generally the following:—



Formation of Ethylic Methyldehydrohexonecarboxylate from Hydric Ethylic Methyldehydrohexonedicarboxylate.

Hydric ethylic methyldehydrohexonedicarboxylate when heated is easily decomposed with evolution of carbonic anhydride and formation of ethylic methyldehydrohexonecarboxylate, thus:—

$$C_6H_8O{<}\begin{matrix}COOH\\COOC_2H_5\end{matrix} = C_6H_8O{<}\begin{matrix}H\\COOC_2H_5\end{matrix} + CO_2.$$

In carrying out this decomposition, the pure acid ethylic salt is transferred to a Wurtz flask and gradually heated in a metal-bath to 200° until the evolution of carbonic anhydride ceases. The resulting oil when fractioned, distils constantly between 223° and 225°, and is pure ethylic methyldehydrohexonecarboxylate.

Analysis.

0·1519 gram of substance gave 0·1135 gram H_2O and 0·3526 gram CO_2

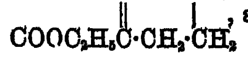
	Theory $C_9H_{14}O_3$.	Found.
C......	63·53 per cent.	63 26 per cent.
H......	8·24 ,,	8·22 ,,
O......	28·23 ,,	28·52 ,,

As it was important to be sure of the identity of this ethereal salt, it was converted into the corresponding acid by hydrolysis with alcoholic potash (as described under the heading "Methyldehydrohexonecarboxylic Acid," p. 715). The acid obtained after recrystallisation from benzene melted at 119—120°, and gave the following numbers on analysis:—

0 1764 gram substance gave 0·1132 gram H_2O and 0·3810 gram CO_2.

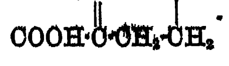
	Theory. $C_7H_{10}O_3$.	Found.
C......	59·15 per cent.	58·90 per cent.
H......	7 04 ,,	7·12 ,,
O......	33·80 ,,	33·98 ,,

The formation of ethylic methyldehydrohexonecarboxylate from hydric ethylic methyldehydrohexonedicarboxylate not only shows the close relation existing between these two substances, but also proves conclusively that the acid ethylic salt mentioned above must have the formula



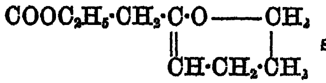
$$\begin{matrix}COOH{\cdot}CH_2{\cdot}C{\cdot}O{-}CH_2\\ \| \qquad | \\ COOC_2H_5C{\cdot}CH_2{\cdot}CH_2\end{matrix}$$

, and not



$$\begin{matrix}COOC_2H_5{\cdot}CH_2{\cdot}C{\cdot}O{-}CH_2\\ \| \qquad | \\ COOH{\cdot}C{\cdot}CH_2{\cdot}CH_2\end{matrix}.$$

In the latter case on elimination of carbonic anhydride an ethereal salt of the formula



$$\begin{array}{l} COOC_2H_5\cdot CH_2\cdot C\cdot O\text{——}CH_2 \\ \qquad\qquad\qquad\ \ \| \qquad\quad | \\ \qquad\qquad\qquad CH\cdot CH_2\cdot CH_2 \end{array}$$

should be obtained; this would be isomeric, and not identical, with ethylic methyldehydrohexonecarboxylate.

Action of Water on Methyldehydrohexonedicarboxylic Acid.

In the introduction it was mentioned that methyldehydrohexonedicarboxylic acid when boiled with water was decomposed into acetobutyl alcohol and two molecules of carbonic anhydride, thus:—

$$C_6H_8O<\begin{smallmatrix}COOH\\COOH\end{smallmatrix} + H_2O = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + 2CO_2.$$

About 5 grams of the pure acid was dissolved in a small quantity of hot water and the solution then heated to boiling in a flask connected with a reversed condenser until the evolution of carbonic anhydride had ceased. The resulting liquid was saturated with anhydrous potassic carbonate, the oil thus precipitated extracted about ten times with pure ether, the ethereal solution dried over potassic carbonate, filtered, and the ether distilled off. In this way a colourless syrup was obtained, which, after standing for some time over sulphuric acid in a vacuum to free it from traces of ether, gave the following approximate numbers on analysis:—

0·1314 gram substance gave 0·1206 gram H_2O and 0·3041 gram CO_2.

	Theory. $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C	62·07 per cent.	63·11 per cent.
H	10·34 "	10·19 "
O	27·59 "	26·70 "

Owing to the small amount of material at my disposal it was not possible to purify this ketone alcohol by fractional distillation, but a qualitative comparison of the substance obtained as above with a specimen prepared from methyldehydrohexonemonocarboxylic acid (p. 715) showed conclusively that the two were identical. In order to be sure that the reaction really took place according to the equation just given, a determination was made of the amount of carbonic anhydride evolved when a definite amount of the acid was decomposed by boiling with water, with the following results:—

2·4811 gram substance gave 1·1432 gram CO_2. Theory for $2CO_2$ = 47·32 per cent. Found 46·07 per cent.

The amount of acetobutyl alcohol formed was not determined.

The principal part of this research was carried out in Professor A. v. Baeyer's laboratory in Munich. Through the kindness of Professors Roscoe and Dixon, I was subsequently enabled to fill in some of the details at the Owens College, Manchester.

LXXV.—*On Aluminium in the Ashes of Flowering Plants.*

By Hikorokuro Yoshida, F.C.S., Assistant Professor of Chemistry, College of Science, Imperial University, Tokyo, Japan.

It has long been known that lycopodium contains aluminium (as acetate) dissolved in its juices, and quite recently the presence of much alumina in the ash of another cryptogamous plant has been announced, although the evidence does not seem quite satisfactory. The occurrence of this element in the ashes of phanerogamous plants, however, has hitherto been attributed to particles of soil adhering to the plants submitted to calcination. Accordingly, in ash analyses, even when elaborate, no mention is found of its presence as a constituent of the real ash, and A. H. Allen's statement, in his *Commercial Organic Analysis* (vol. I, p. 38), that "flowering plants do not contain aluminium as a normal constituent," appears to express the current opinion of chemists.

At least two exceptions to the supposed non-occurrence of aluminium in phanerogamous plants, have, however, been noticed by myself (*Journ. Chem. Soc.*, **43**, Trans., 1883, 481) and quite recently by M. L'Hôte (*Compt. rend.*, **104**, 853).

In the aqueous part of the latex of *Rhus vernicifera*, the lacquer tree of Japan, aluminium is present in solution, apparently as arabate, for on treating the latex with absolute alcohol, boiling the precipitate thus formed with water, filtering and evaporating the aqueous extract, a residue of gum was obtained, which when burnt left 5 per cent. ash, containing 7·8 per cent. of its weight of alumina.*

L'Hôte's recognition of aluminium as a normal constituent of a flowering plant was made in the juice of the grape, all samples, except one of the fresh fruit and of wine, examined by him, having yielded alumina in small quantity.

---

* As recorded by me at the time in the Journal of the Chemical Society. Since then, however, I have determined the phosphoric acid, which I had regarded as present in too small quantity to need estimation, and as I now find it to be more considerable than I thought; I believe that 6·3 per cent. more closely expresses the proportion of alumina than 7·8 per cent. as formerly stated. At the first opportunity, I shall redetermine it.

There being little or no evidence, except my own, as to whether aluminium is or is not to be ranked among the mineral constituents of flowering plants, I undertook, at the suggestion of my respected colleague, Dr. Divers, to make a few careful examinations of some beans and grains, in order, if possible, to decide the matter. These were completed two or three months ago, and before the notice in the *Chemical News* of L'Hôte's interesting observations, or the number of the *Comptes rendus* containing them had come to hand.

The fact that the soil of the plain of Musashi, in which Tokyo is situated, and which is of volcanic origin, is remarkable for the large proportion of alumina in it soluble in hydrochloric acid, gave promise that, if anywhere, then certainly here, would aluminium be found in flowering plants.

The samples examined, for which I have to thank Dr. O. Kellner, had been grown on the farm lands of the Imperial College of Agriculture, at Komaba, near Tokyo. Each one was carefully picked over, and all imperfect and visibly soiled grains rejected.

The peas and beans were soaked and well washed in water. Some of these were rubbed with cloths, and left to dry in the air and sun. The rest were, in their soddened state, broken up by hand in water into hull and cotyledons, the two carefully separated and then dried on filter-paper in the sun.

The rice (hulled),* barley, two millets and buckwheat were also picked over, and were then bruised in an iron mortar, winnowed, washed, rubbed on a sieve until the water passing through showed scarcely any turbidity, and then dried on sheets of paper in the sun. The calcination was carried out in large platinum dishes, 100 grams at a time, and in most cases several such quantities of the prepared sample were burnt, and the ashes mixed and ground together in an agate mortar. The peas, beans, and buckwheat were calcined from first to last over the lamp.

Rice, wheat, and the rest being more difficult to calcine, the samples were charred and partially burnt over the lamp, and then the dish transferred to a capacious blind muffle to complete the calcination. The muffle was kept nearly closed and at as low a temperature as possible. It was of clay, but well seasoned by work, and the dishes were always removed, when charcoal had to be added to the fire, or when the muffle was heating in the morning and cooling at night, and every other care taken that no contamination with clay or charcoal ash should occur. Generally the calcination was effected with but little fusion of the ash. The prepared ash was boiled with dilute hydrochloric acid and evaporated completely to dryness, again treated with dilute hydrochloric acid, and filtered through ash-free paper. The residue was washed, calcined, and weighed.

---

* Even the best hulled rice of commerce has in this country adhering to it some of the dust which has been employed in polishing the grains after hulling, and thus rendering them translucent. This dust or powder is Boshū sand, a white tufa containing 10—12 per cent. of alumina.

The filtrate, nearly neutralised, and mixed with sodium acetate (in which aluminium could not be detected), was boiled and filtered through ash-free paper and the precipitate washed. The precipitate was washed off into a platinum dish, and digested with sodium hydroxide, which I had prepared from sodium in a platinum dish. The filtered solution was acidified with hydrochloric acid and precipitated with ammonia. The precipitate was washed, dried, and ignited, and regarded as aluminium phosphate. In one or two cases, its composition was verified by determining the phosphoric acid in it.

In another part of the ash, the total phosphoric acid was estimated by precipitation as ammonium phosphomolybdate and weighing as magnesium pyrophosphate.

In the following table, there are included the numbers found for percentage of ash in the grains, and of phosphoric acid and silica in the ash, because they serve to show the normal character of the samples and of my analyses.

	Ash per cent of air-dried sample.	Per cent. of ash of		
		Alumina.	Phosph. acid.	Silica, &c.
Pea (whole), *Soja hispida*........	—	0·053	33·48	—
Pea (cotyledons)	4·22	0·000	—	0·50
Pea (hull or skin)	4·31	0·268	5·66	3·60
Red bean (*Azuki*), *Phaseolus radiatus*....................	2·60	0·096	32·89	0·25
Rice (hill)......................	0·87	0·161	51·33	9·86
„ (paddy)	0·56	0·189	52·79	10·09
Wheat	2·62	0·106	65·55	1·81
Barley	1·09	0·140	33·19	1·19
Millet (*Awa*), *Panicum italicum*...	1·68	0·272	40·43	8·91
„ (*Hiyé*), *P. crus-corvi*......	0·94	0·185	39·87	8·62
Buckwheat....................	1·72	0·113	1·91	0·81

From this table, it will be seen that I have found alumina in every case except in that of the cotyledons of the pea, while in the hull or skin of the pea, one of the largest amounts of alumina occurs. The results here recorded may at least serve to indicate the propriety of reconsidering the accuracy of the dictum that aluminium is not a constituent of flowering plants.

LXXVI.—*Some Organic Vanadates.*

By John A. Hall, Owens College.

The analogy existing between the vanadates of the alkalis on the one hand and the arsenates and phosphates on the other has been shown by Roscoe, Baker (*Chem. Soc. Journ.*, Trans., 1885, 353), myself (this vol., p. 94), and others.

The ethereal salts of phosphoric and arsenic acids have been well investigated, but no work seems to have been published as yet, on the ethereal salts of vanadic acid; I therefore undertook the preparation and investigation of these compounds, with the following results. The ortho-vanadates of the alkyl series, with the exception of the methyl-derivative, can be easily prepared by the action of alkyl halogen-compounds on silver orthovanadate. They are yellow liquids, which decompose on distillation under the ordinary pressure, but the lower members of the series can be distilled under reduced pressure. On addition of water, hydrated vanadic acid is precipitated; no evidence whatever was obtained of the existence of acids corresponding to the ethylphosphoric acids.

The pyro-vanadates of the lower members have not been obtained in sufficient quantity for analysis, they appear to decompose as represented by the equation $R_4V_2O_7 = 2R_2O + V_2O_5$.

The meta-vanadates have not been obtained at all.

It appears that the alkyl ortho-vanadates are more stable than the pyro- or meta-compounds, whilst the inorganic metavanadates are the most stable, and that the organic vanadates resemble the corresponding arsenates more closely than the phosphates.

I. *Methyl Vanadates*, $(CH_3)_3VO_4$?

When silver ortho-vanadate is heated for some hours with rather less than the theoretical quantity of methyl iodide, diluted with ether or benzene, the solid product is found to contain silver iodide and vanadic anhydride, but the liquid contains very little vanadium; evidently methyl vanadate has been formed and decomposed thus:—

$$3CH_3I + Ag_3VO_4 = (CH_3)_3VO_4 + 3AgI,$$
$$2(CH_3)_3VO_4 = V_2O_5 + 3(CH_3)_2O.$$

By no modification of the experiment have I been able to obtain the above compound in quantity.

II. *Ethyl Orthovanadate*, $(C_2H_5)_3VO_4$.

This substance is easily obtained by heating together silver orthovanadate and the theoretical amount of ethyl bromide diluted with ether; ethyl iodide can be used instead of the bromide, but it is then necessary to use a slight excess of the silver salt, or much free iodine is obtained, which renders the purification of the product almost impossible.

It is easy to see that a reaction takes place by the change in shade of the silver salt.. On evaporating the now yellow ethereal liquid, a dark yellow residue is left which distils under a pressure of 120 mm., between 149·5 and 151° (uncorrected).

Analysis.—The vanadium was determined by decomposing a quantity of the substance with water and repeatedly evaporating to dryness with water (to remove alcohol), reducing by means of sulphur dioxide, and then reoxidising with standard permanganate solution. The carbon and hydrogen were determined by combustion.

	Calculated for $(C_2H_5)_3VO_4$.	Found.	
C........	35·6	35·15	
H.......	7·41	7·54	
V_2O_5	45·05	45·29	45·4

The vapour-density of the substance was ascertained to be almost exactly 200 (calculated for $(C_2H_5)_3VO_4 = 202·2$), using Hofmann's apparatus and pseudocumene in the outer tube.

The sp. gr. was found to be 1·167 at 17·5° C.

Its refractive indices are—

For lithium line	(6·708 wave-length)........	1·473
„ sodium „	(5·895 „)........	1·481
„ thallium „	(5·439 „)........	1·483

Applying these figures to the formula $\left(\frac{A^2_\infty - 1}{(A^2_\infty + 2)d}\right)M$,* we obtain 46·7 as the refractive equivalent of this compound.

I have determined the refractive indices of ethyl phosphate and ethyl arsenate.

They are—for the phosphate—

For lithium line	1·404
„ sodium „	1·406
„ thallium „	1·408

---

* A_∞ = refractive index for theoretical wave of infinite wave-length.
d = specific gravity.
M = molecular weight.

For the arsenate—

For lithium line	1·437
„ sodium „	1·440
„ thallium „	1·442

Using the above formula, we obtain 40·7 as the refractive equivalent for ethyl phosphate, and 43·7 as that for ethyl arsenate.

III. *Propyl Vanadate*, $(C_3H_7)VO_4$

This substance was obtained in a manner corresponding with that used for the preparation of ethyl vanadate, which it resembles closely.

Analysis.

	Calculated for $(C_3H_7)_3VO_4$.	Found
V_2O_5	37·3	37·5

IV. *Butyl Vanadate*, $(C_4H_9)_3VO_4$.

A slight excess of silver vanadate was heated with primary butyl bromide and ether. The product resembles the compounds previously described, but it cannot be distilled.

The analysis yielded the following numbers:—

	Calculated for $(C_4H_9)_3VO_4$.	Found.
C	50·35	49·9
H	9·44	9·2
V_2O_5	31·88	32·1

V. *Amyl Vanadate*, $(C_5H_{11})_3VO_4$.

When excess of silver vanadate is heated with amyl bromide, using either ether or benzene as a diluent, this compound is formed. It is a yellow liquid from which it is very difficult to remove the smell of amyl bromide; this is best accomplished by heating it under reduced pressure, and at the same time allowing a stream of dry air to pass through it.

Amyl vanadate decomposes on distillation The residue contains vanadium tetroxide and carbon, it also decomposes on standing, depositing a light yellow powder, which, however, has not yet been obtained in sufficient quantity for analysis.

The analysis was conducted as in the other cases.

	Calculated for $(C_5H_{11})_3VO_4$.	Found.
C	54·84	54·53
H	10·05	10·1
V_2O_5	27·75	28·1

VI. *Ethyl Pyrovanadate*, $(C_2H_5)_4V_2O_7$?

When ethyl bromide is heated with silver pyrovanadate and ether, a reaction begins after some hours, the ether becomes slightly yellow, and on distilling it off a small quantity of a dark-yellow liquid smelling like the orthovanadate is left. I have been unable to so modify the experiment as to obtain sufficient of the liquid for analysis.

Similar results were obtained with the other alkyl halogen-compounds, but in the case of amyl the yield was sufficient for analysis.

VII. *Amyl Pyrovanadate*, $(C_5H_{11})_4V_2O_7$.

This can be prepared as above; the product is a very dark yellow liquid smelling strongly of amyl-compounds, it was therefore treated like the other amyl-derivatives described, but I was unable to free it completely from amyl ether.

The analysis gave the following figures :—

	Calculated for $(C_5H_{11})_4V_2O_7$.	Found.
C	48·17	48·8
H	8·83	8·7
V_2O_5	36 57	36·2

The substance solidifies after a few days, probably decomposing.

When alkyl halogen-compounds are heated with silver metavanadate, no organic vanadate is obtained; as the silver residue always contains a halogen and is mixed with vanadic anhydride, it appears that the reaction may be represented thus :—

$$RCl + AgVO_3 = RVO_3 + AgCl,$$
$$2RVO_3 = R_2O + V_2O_5.$$

When benzyl chloride is heated with silver vanadate, the product consists of benzaldehyde, benzyl oxide, vanadium tetroxide and pentoxide and silver chloride. This reaction can be expressed by the equations—

$$3C_6H_5{\cdot}CH_2Cl + Ag_3VO_4 = (C_6H_5{\cdot}CH_2)_3VO_4 + 3AgCl,$$
$$2(C_6H_5{\cdot}CH_2)_3VO_4 = 3(C_6H_5{\cdot}CH_2)_2O + V_2O_5,$$
$$(C_6H_5{\cdot}CH_2)_2O + 2V_2O_5 = 2C_6H_5{\cdot}CHO + 2V_2O_4 + H_2O.$$

VIII. *Methyl Phosphate*, $(CH_3)_3PO_4$.

As I was unable to obtain methyl vanadate, and methyl phosphate had not been described, I tried the action of methyl iodide on silver orthophosphate, and obtained a colourless liquid boiling at 190° (uncorrected) under the ordinary pressure without decomposition. It dissolves in water without immediate formation of phosphoric acid.

A combustion gave the following:—

	Calculated for $(CH_3)_3PO_4$.	Found.
C	25·7	25·55
H	6·42	6 23

Thus in no way accounting for the non-existence of the methyl vanadate.

LXXVII.—*Evaporation and Dissociation.* Part VII. *A Study of the Thermal Properties of a Mixture of Ethyl Alcohol and Ethyl Oxide.*

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

IT has been shown in Part VI of this series of memoirs (*Phil. Mag.*, 1887, May, p. 435, and Aug., p. 196), that for both the gaseous and the liquid states the relation of pressure to temperature at constant volume may, in the case of methyl and ethyl alcohols, ethyl oxide, and carbon dioxide, and presumably in the case of all stable liquids, be expressed by the formula $p = bT - a$. That is, the isochoric lines, or lines of equi-volume for unit mass of the substance, are straight when mapped against pressures as ordinates and temperatures as abscissæ. We also showed that with the two dissociating substances, acetic acid and nitric peroxide, such isochoric lines are not straight, but are, at large volumes, tangential to the theoretical isochoric lines of minimum density at high temperatures, and at lower temperatures probably tangential to the theoretical isochoric lines of maximum density. A comparison of the behaviour of such stable and dissociable substances has shown the effect of chemical union on the relations of pressure, temperature, and volume.

But the mixture of two liquids, such as alcohol and water, is known frequently to be accompanied by contraction and by evolution of heat. It therefore appeared of interest to investigate thoroughly the behaviour of such a mixture, in order to throw light on the nature of this attraction.

Such a mixture must, in our opinion, be regarded as a solution of the one liquid in the other, and the meaning of the word "solution" must be so extended as to cover such instances. For while we speak of the "solution" of a solid in a liquid, and of the "solution" of a gas in a liquid, it is customary to speak of the "mixture" of two liquids. A solid paraffin, of definite formula for example, dissolves in a liquid paraffin of lower molecular weight; but the solid paraffin may be melted, and then mixed with the liquid, and it cannot be denied that the end result is identical in both cases. It happens that it is, as a rule, impossible to mix a fused salt with liquid water; but that is owing merely to the difficulty of obtaining water at a sufficiently high pressure and temperature. Mr. Shenstone has recently shown that with the easily fusible salt, silver nitrate, mixture with water at high temperatures takes place in any desired proportion. The following results, we think, may therefore throw light on the vexed question of solution.

For a description of our apparatus and methods, we must refer to our memoir on ethyl oxide (*Phil. Trans.*, 1887, Part I, p. 57).

In filling the experimental tube, an attempt was made to obtain molecular proportions of ether and alcohol. A mixture of these liquids, weighed out in the desired proportions, was introduced by means of a pipette into the little apparatus, displacing the mercury with which the apparatus had been filled; a woodcut of this apparatus is shown on p. 61 of our memoir on ether (*loc. cit.*). After the mercury had been removed in great part by a Sprengel's pump, the exit from the bulb was sealed. There was, therefore, practically no air in the bulb or the experimental tube, its space being occupied by the mixed vapours. The liquid in the experimental tube was then repeatedly boiled in the usual manner, so as to displace the air-film adhering to its walls. We supposed that we had then the desired mixture in our tube. But data will be produced to prove that during the process of boiling, ether had escaped in greater proportion than alcohol; hence our final proportion was not molecular, but in the ratio of 63 mols. of alcohol to 37 mols. of ether.

The pressures were measured by two gauges, as usual, but the low pressure gauge was separately controlled (and its indications subsequently transferred to the high pressure gauge) by direct comparison of several readings against a column of mercury of known height and temperature. The comparison is as follows:—

Calculated. mm.	Found by direct reading. mm.
1008·7	1005·0
1182·8	1180·4
1299·9	1299·6
1339·9	1337·5

The mean difference is 0·2 per cent., and by taking the mean of all the readings we assume that the probable error is not above 0·1 per cent.

The specimens of alcohol and ether were specially prepared as described in our former paper, and were dried finally with sodium. The boiling points, as before, were absolutely constant.

EXPERIMENTAL RESULTS.

Vapour-pressures.

As the vapour-pressures of a mixture of liquids is a function of the relative volumes of liquid and gas, we were precluded from experiments of this nature. There is no true vapour-pressure, and in the diagram on Plate II representing isotherms the lines corresponding to the vapour-pressures of a pure substance are given; and it is evident that with the mixture the pressure rises with decrease of volume. The vapour-densities at low temperatures were also omitted, inasmuch as the behaviour of such a mixture at low temperatures is deducible from measurements at higher temperatures and pressures.

Constants at High Temperatures.

This series includes a few determinations of compressibility at low temperatures. The usual corrections were employed for volume, pressure, and temperature, for details concerning which our memoir on ether may be consulted (*loc. cit.*, p. 65).

As before, three quantities were employed; the largest occupying 0·3558 c c. at 13·5°; the middle quantity, 0·04765 c c. at 15 6°; and the smallest quantity, about one-tenth of the middle quantity. With the largest quantity, the expansion of the liquid and the compressibility were measured; with the middle quantity, the behaviour at temperatures ranging between 190° and 275°, as regards pressure, temperature, and volume, both as liquid and gas; and with the smallest quantity, from 80° up to 275°, similar data were obtained for the gas. These measurements cover all the relations of pressure, temperature, and volume, from 350 c.c. per gram, down to 1·3 c.c per gram.

So far, the two bodies had remained mixed. At 210°, the volume was increased as much as possible, in order to ascertain whether total evaporation would take place. The effect of this was to partially separate the alcohol from the ether, the more volatile ether occupying the top of the tube, while the less volatile alcohol remained mostly in the state of liquid. It will be seen from the numbers (p. 759), and from the diagram (Plate I), that the volumes are much influenced by mixture.

Measurements with the Largest Quantity. (Plate I.)

Temp.	Pressure.	Vols. of 1 gram.	Temp.	Pressure.	Vols. of 1 gram.
	mm.	c.c.		mm.	c.c.
20°	1500	1·3197	140°	9300	1·6309
	9559	1·3171		10880	1·6295
	43306	1·3105		16370	1·6229
30	800	1·3365		22050	1·6163
	22020	1·3306		27360	1·6094
	48800	1·3242		34130	1·6030
40	800	1·3540		39760	1·5964
	11630	1·3506	150	11890	1·6768
	33510	1·3441		17040	1·6695
50	800	1·3720		21470	1·6630
	6880	1·3706		25850	1·6562
	26890	1·3641		30780	1·6497
	51280	1·3576		35740	1·6430
60	800	1·3931		40870	1·6364
	7535	1·3904		46500	1·6299
	26560	1·3839	160	14180	1·7354
	46400	1·3772		16680	1·7294
70	1000	1·4159		19670	1·7227
	11620	1·4106		23120	1·7161
	26560	1·4040		26270	1·7095
	44210	1·3976		29850	1·7028
80	2291	1·4348		34280	1·6962
	11910	1·4303		38210	1·6896
	22410	1·4237		42510	1·6830
	40330	1·4173		46510	1·6764
90	2863	1·4608	170	17010	1·8015
	5305	1·4581		18470	1·7962
	10920	1·4570		20650	1·7896
	22040	1·4502		23300	1·7830
	36030	1·4436		25860	1·7763
100	3679	1·4889		28200	1·7697
	5950	1·4861		30050	1·7630
	13240	1.4836		33630	1·7564
	23340	1·4769		36840	1·7498
	35010	1·4704		39800	1·7432
110	4730	1·5199		42120	1·7366
	8070	1·5166		46400	1·7299
	17810	1·5099		50150	1·7233
	27330	1·5045	180	22240	1·8710
	38530	1·4969		24280	1·8630
120	5925	1·5511		26020	1·8564
	9300	1·5498		27530	1·8497
	17020	1·5432		29360	1·8430
	24400	1·5366		31200	1·8364
	34400	1·5300		33480	1·8297
	43300	1·5234		35500	1·8232
130	6745	1·5895		38160	1·8166
	13640	1·5828		39970	1·8100
	20840	1·5762		42630	1·8033
	27370	1·5696		44890	1·7966
	34760	1·5629		47800	1·7900
	42870	1·5564	190	25700	1·9770

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	cc.
190°	27450	1·9635	200°	32430	2·0864
	29870	1·9501		33560	2·0711
	31930	1·9368		34810	2·0576
	34680	1·9234		36260	2·0443
	37200	1·9100		37840	2·0309
	40140	1·8969		39450	2·0175
	43390	1·8835		41300	2·0040
	46970	1·8702		43340	1·9907
200	30940	2·1047		45490	1·9778
	31410	2·0980		47860	1·9639

The following series may be held to relate to partially separated liquids:—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
210°	35820	2·3272	210°	37850	2·2434
	35860	2·3150		38980	2·2201
	36200	2·3014		40160	2·1981
	36840	2·2742			

This series formed the conclusion of a day's work. The tube was necessarily allowed to cool, and again heated up, when thorough mixture was obtained by the violent convection currents. A repetition gave the following numbers:—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
210°	34880	2·3096	210°	40920	2·1795
	35570	2·2877		42910	2·1526
	36520	2·2606		45220	2·1256
	37650	2·2337		47790	2·0986
	39180	2·2066		51090	2·0717

The volume was then greatly increased, so as to reproduce a separation. On compressing to a small volume, no meniscus was visible, owing to the fact that the ether, which had now accumulated at the top of the tube, was above its critical temperature. Two readings were taken here. The pressure being 37810 mm., the volume was

2·5456 c.c. per gram, and at 38140 mm. the volume was 2·4778 c.c. The volume was again increased to about 4·5 c.c. per gram, and again decreased.

The following series was obtained:—

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
°	mm.	c.c.	°	mm.	c.c.
210	37070	2·5456	210	43650	2·1796
	37640	2·4099		45380	2·1526
	39700	2·2877		47400	2·1256
	40450	2·2607		49850	2·0986
	41230	2·2337		52570	2·0717
	42400	2·2066			

The volume was then slightly increased, and a few readings were taken.

Pressures	40350 mm.	39530 mm.	37610 mm.
Volumes	2·2607 c.c.	2·2877 c.c.	2·4099 c.c.

It is evident that these readings closely correspond with those of the last series.

The liquid was then allowed to cool partially, and then heated again. Partial mixture had taken place.

Pressure.. 39750 mm. Volume.. 2·2607 c.c. (A).

The process was repeated, and the following readings taken:—

Pressures	39510 and 39350 mm.
Volumes	2·2580 „ 2·2594 c.c. per gram.

These are indicated on the diagram, Plate II, as (B).

After a further separation had been effected by heating the lower portion of the tube, while allowing the upper portion to cool, the volume being large in order to favour distillation, the temperature was equalised, and the volume reduced. It was then found that in addition to the meniscus formed by the alcoholic ether at the top of the liquid, a second meniscus was visible at the junction of the two heterogeneous liquids. Two readings were taken; and it will be seen that the pressure corresponding to these volumes is much higher than previously.

Pressures......	40570 mm.	41340 mm. (C).
Volumes	2·2877 c.c.	2·2607 c.c. (C).

By suitable heating, a partial mixture was obtained, and the following readings taken:—

Pressures	39450 mm.	38490 mm. (D).
Volumes	2·2607 c.c.	2·2871 c.c. (D).

The volume was lastly kept small, to prevent boiling, and the upper part of the tube was cooled. The meniscus at the division of the ether and alcohol was seen to descend the tube, until it became lost at the surface of the mercury. The whole of the tube was again heated, and readings were taken.

Pressures	36670 mm.	35520 mm. (E).
Volumes	2·2607 c.c.	2·2877 c.c. (E).

It will be seen that these readings agree perfectly with those of the second series.

It is obvious from these observations, that the volume of the substances when thoroughly mixed is smaller than when they are separate, under these conditions of temperature and pressure. On increasing the volume slightly, the meniscus at the top of the thoroughly mixed liquids was perfectly visible, and there was no sign of junction in the body of the liquid. Experiments were also made at 220° with partial mixture, and with complete mixture, with the same general results, although much less marked.

Series I.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
220°	39130	3·7160	220°	39310	3·4441
	39160	3·6180		39460	3·3761
	39200	3·6201		39530	3·3081
	39230	3·5123		39570	3·2269

Series II.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
220°	44860	2·4106	220°	50500	2·2750
	45700	2·3835		48960	2·3021
	46590	2·3563		47640	2·3292
	47740	2·3292		46590	2·3563
	48960	2·3021		45710	2·3835
	50500	2·2750		44860	2·4106
	52140	2·2478		43170	2·4785

Series II.

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
220°	41950	2·5522	220°	39280	3·2269
	41150	2·6143		39360	3·0908
	40550	2·6826		39670	2·9549
	39800	2·8189		39820	2·8189
	39410	2·9549		40230	2·7508
	39340	3·0908		40650	2·6826
	39200	3·2269		41340	2·6143
	39130	3·3761		42150	2·5522
	39110	3·6480		43370	2·4785
	39220	3·5123		45090	2·4106
	39180	3·4480		39120	3·6480
	39220	3·4123		39130	4·3319
	39260	3·3761			

After the second last measurement was taken, the volume was increased and a small quantity of liquid appeared at the bottom of the tube; on still further enlarging the volume, this liquid increased, and then began to decrease. If the volume was increased very slowly to the same amount, no liquid appeared. This behaviour is probably due to cooling and consequent separation of alcohol.

Measurements with the Middle Quantity. (Plate II.)

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
190°	13370	32·41	190°	21570	16·04
	13700	31·37		22070	15·00
	14 80	30·35		22370	14·00
	14460	29·33		22620	13·00
	14860	28·33		22820	12·01
	15270	27·29		23060	11·04
	15690	26·27		23210	10·06
	16170	25·25		23340	9·070
	16680	24·14		23560	8·092
	17180	23·12		23640	7·113
	17750	22·11		23870	6·136
	18310	21·09		24000	5·163
	18900	20·06		24200	3·218
	19530	19·04		24330	2·250
	20190	18·04		24780	1·961
	20870	17·02			

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
200°	29300	2 089	200°	26410	12·02
	30760	2 069		27060	11·04
	13850	32·42		27300	10·06
	14600	30 36		27570	9·072
	15430	28·31		27680	8·094
	16350	26·28		27910	7·115
	17410	24 15		28020	6·138
	18580	22·11		28130	5·164
	19840	20 07		28330	4·189
	21300	18 04		28410	3·219
	22840	16 02		28740	2 250
	24610	14 00			
210	33670	2·314	210	26070	14·01
	35610	2 267		28210	12·03
	34650	2 298		30540	10 07
	14340	32 41		31630	9·077
	15130	30·38		32590	8·099
	16010	28·33		32860	7 120
	16970	26·29		32900	6·143
	18120	24·17		33060	5·167
	19350	22 12		33340	4·192
	20750	20 08		33380	3·224
	22310	18·05		37200	2·253
	24070	16 03			

At 219·5°, with small volumes, no meniscus was visible, and the substance became clouded on slightly increasing volume, presenting the usual appearance of a body at its critical point. On still further increasing volume, a permanent meniscus appeared. It appears therefore that 219·5° is the critical temperature of this particular

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm	c.c.
220°	14800	32 45	220°	31150	9·075
	15630	30·39		35600	8·099
	16540	28 34		36820	7·120
	17570	26·30		38050	6·140
	18790	24 17		38830	5·167
	20090	22·13		38960	4·192
	21600	20 08		39510	3·219
	23350	18·05		40420	2·736
	25230	16 03		42110	2 541
	27480	14 01		43850	2·444
	29980	12·03		46280	2·349
	32770	10·07		51390	2·251

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
230°	15270	32·44	230°	34730	10·07
	16130	30·38		36540	9·080
	17100	28·34		38240	8·102
	18170	26 30		40140	7·123
	19450	24 17		41800	6·146
	20830	22·13		43310	5·173
	22450	20·08		44840	4·193
	24230	18 06		46410	3·224
	26390	16·03		49710	2·736
	28840	14·01		51050	2·638
	31610	12·02		47730	2·929
240	38810	9·080	240	48070	5·172
	41050	8·102		50680	4·192
	43200	7·123		52060	3·709
	45620	6·146		54340	3·224
250	16130	32·46	250	31340	14·02
	17090	30·40		34720	12 03
	18120	28·35		38770	10·07
	19310	26·29		41100	9·080
	20710	24·18		43710	8·102
	22230	22·15		46160	7·123
	24000	20·10		49340	6·146
	26100	18·07		52590	5·173
	28480	16·04			
275	17150	32·48	275	31060	16·05
	18230	30·42		34380	14·03
	19350	28·37		38440	12·04
	20650	26·33		43100	12·09
	22250	24·20		46280	9·090
	23900	22·15		49820	8·110
	25870	20·11		53930	7·129
	28220	18·08			

mixture. On increasing volume, the relative amount of alcohol in the liquid is increased, when the critical temperature would be higher.

Measurements with the Smallest Quantity.

Temp.	Pressure.	Vol of 1 gram.	Temp.	Pressure.	Vol of 1 gram.
	mm.	c c.		mm.	c c
80°	1042	350·3	80°	1422	129 9
	1104	306·0		1496	108·7
	1150	273 0		1590	87·47
	1195	238 9	liquid present	1705	66 35
liquid present	1228	216·9		1763	55 81
	1263	194 9		1830	45 28
	1306	173 1		1899	31 78
	1360	151·3		1978	24 31
100°	1158	350·5	100°	2397	130 0
	1317	306·1		2493	108 8
	1468	273·1		2619	87 54
	1665	239 0	liquid present	2784	66 40
	1822	217·0		2885	55·85
	2012	195·0		2996	45 32
	2188	173 2		3112	34·81
	2305	151·4		3239	24·33
130	1263	350 7	130°	3237	130·1
	1439	306·4		3808	108·8
	1608	273 3		4619	87 58
	1827	239·2		5573	66 43
	2004	217·2		5835	55 88
	2220	195·1	liquid present	6022	45·31
	2483	173 3		6270	34 82
	2808	151 5		6543	24·34
160	1344	355·1	160°	3498	131·7
	1533	810·2		4136	110·2
	1714	276·8		5054	88·69
	1949	212 3		6470	67·25
	2114	219·9		7519	56·58
	2373	197·6		8961	45·91
	2604	175·5		10975	35·26
	3027	153·4			
170	1393	351·1	170	4306	108·9
	1500	306·7		5266	87·66
	1778	273 6		6751	66·49
	2045	239·4		7873	55·93
	2227	217·4		9409	45 38
	2465	195·3		11612	34·86
	2765	173 5		13081	29·62
	3143	151·7		14939	24·37
	3643	130·2			

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol. of 1 gram.
	mm.	c.c.		mm.	c.c.
180°	1424	351·2	180°	4431	109·0
	1628	306·7		5398	87·68
	1827	273·7		6981	66·50
	2074	239·5		8137	55·94
	2280	217·4		9748	45·39
	2527	195·4		12100	34·87
	2832	173·5		15826	24·38
	3224	151·7		18410	19·13
	3734	130·2			
200	1487	351·3	200	4674	109·0
	1701	306·9		5711	87·73
	1903	273·8		7387	66·54
	2172	239·6		8643	55·97
	2388	217·5		10410	45·42
	2654	195·5		13000	34·88
	2975	173·6		17300	24·39
	3383	151·8		20500	19·13
	3931	130·3			
220	1541	351·5	220	4877	109·1
	1768	307·0		5997	87·77
	1980	273·9		7777	66·57
	2259	239·7		9130	56·00
	2488	217·7		11000	45·44
	2763	195·6		13860	34·90
	3105	173·7		18730	24·40
	3536	151·9		22450	19·14
	4100	130·4			
230	1561	351·6	230	4201	130·4
	1806	307·1		4981	109·1
	2010	274·0		6152	87·79
	2295	239·8		7966	66·58
	2532	217·7		9356	56·01
	2811	195·6		11310	45·45
	3160	173·7		14300	34·91
	3614	151·9		19330	24·41
250	1682	339·0	250	5438	105·1
	1935	296·1		6680	84·65
	2167	264·2		8689	64·19
	2474	231·2		10225	54·00
	2740	209·9		12397	43·82
	3048	189·1		15700	33·66
	3425	167·5		21320	23·53
	3914	146·5		26010	18·46
	4553	125·7			

Temp.	Pressure.	Vol. of 1 gram.	Temp.	Pressure.	Vol of 1 gram.
	mm.	c c.		mm.	c c.
275°	1732	339 2	275°	5706	105 2
	2019	296 3		6958	84 71
	2252	264·4		9213	64 24
	2586	231·4		10810	54 04
	2855	210·1		13290	43 85
	3186	188·8		16710	33 68
	3598	167·6		22920	23 54
	4113	146 6		28100	18 48
	4792	125·8			

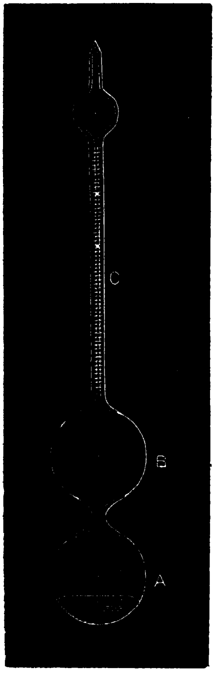
Weight of Substance employed.—To ascertain the volume of 1 gram of the mixture, it is necessary to know the weight. That was obtained by assuming that when the product of pressure and volume is constant, the gases present have their normal density. But the problem of ascertaining the weight is a complex one, inasmuch as the accurate relative proportions of the alcohol and ether are unknown. And it is still further complicated by the fact that on two occasions, small traces of liquid found their way up the experimental tube, thereby increasing the mass of the smallest quantity. There is, however, no possibility of a mistake having occurred by such small additions, for after each day's work the temperature was brought back to that at which the first determinations were made, and identical results were obtained except in the two cases where liquid was seen to ascend. The amount of liquid remained constant at the following temperatures:—160°, 170°, 180°, 200°, 220°, and 230°; and the products of pressure into volume at the largest volumes are as follows:—

160°.	170°.	180°.	200°.	220°.	230°.
1601·3	1639·4	1676·3	1751 7	1815·9	1812 0
1599 3	1634 7	1674 1	1750·0	1820 0	1859 2
1598·3	1630·9	1676·2	1747·2	1818 5	1816 4
—	1641·8	—	1745·0	1815·9	1841·8
Vol. decreased from 4 to 3 between extremes.				1815 6	—
	decrease 3 to 2.	decrease 4 to 3.	decrease 3 to 2.	decrease 8 to 5.	decrease 3 to 2.

It is evident from these numbers that we are justified in regarding the vapour-density as normal. But in order to know the weight, we must know the vapour-density; and in order to ascertain the vapour-density, we must know the relative proportion of each constituent.

The vapour-densities of mixtures of alcohol and ether in the proportions of x molecules of alcohol to $100-x$ molecules of ether were calculated; and also the corresponding weights from the mean value of $\frac{pv}{t}$, and these vapour-densities. The weights were then mapped against values of x. It will be seen later that the true weight was obtained from the intersection of this line with another, which must now be explained.

It was supposed, as has been mentioned, that the tube was originally filled with a mixture of ether and alcohol in molecular proportions. In order to obtain the weight of the largest quantity of mixed liquids in the experimental tube, two methods of determining specific gravity were resorted to; (1) direct determination of the specific gravity of the mixture; and (2) measurement of the contraction on mixing the alcohol and ether in molecular proportions at 0°. From the known specific gravities of the two liquids at 0°, the specific gravity of the mixture can be deduced from the second method. The first method proved unsatisfactory owing to the extreme difficulty, if not impossibility, of filling any form of specific gravity apparatus without evaporating some of the ether; the results obtained were for this reason



always too high. We therefore avoid giving details; but it may be mentioned that the specific gravity found at 12·9°, with all corrections for a vacuum, &c., introduced, was 0·07564. To determine the contraction on mixing, an apparatus (shown in the accompanying woodcut) was employed.

Two bulbs, A and B, communicate by a wide capillary. To the top bulb a graduated stem C was sealed, near the upper end of which a small bulb was blown. The apparatus was calibrated and weighed; and the capacity of the lower bulb was reduced to such an amount by addition of mercury, that the amount of alcohol which it contained up to the constriction at 0°, bore a molecular proportion to the ether contained in the upper bulb and the stem. While the apparatus was kept in melting ice, alcohol was introduced so as to fill the lower bulb to the constriction, and ether was then poured in so as to fill the upper bulb and the stem up to a calculated mark. The upper tube above the small bulb was then closed by sealing. The apparatus now contained alcohol and ether in molecular proportions, unmixed. By inverting and shaking the apparatus, mercury was made to pass repeatedly from one bulb into the other, thus being replaced by the mixed liquids. After 20 inversions, no further contraction took place, and the altered volume was then read, again at 0°. The following results were obtained:—

First measurement......	0·725	per cent. contraction.
Second "	0·731	" "
Mean............	0·728	" "

With 0·728 per cent. contraction, the specific gravity of the mixture is 0·7671, and its specific volume, 1·3036, the specific volume of alcohol at 0° being taken as 1·2403, and that of ether 1·3583 (see our previous memoirs on alcohol and ether). It has been assumed that the percentage contraction does not greatly vary when the proportions of alcohol and ether are considerably altered. We are justified at least in supposing that the result of the following calculations, giving the weight, would not be appreciably affected.

The next step was to obtain the ratios of the weights of the second and third quantities to the first, by comparison of the volumes at the same temperatures and pressures, both in the liquid and gaseous states with the smallest quantity; and in the gaseous state with the smallest quantity. The following ratios were obtained between the largest and middle quantities:—

Ratios.—0·13235; 0·13096; 0·13256; 0·13218; 0·13385; 0·13524; 0·13362; 0·13333; 0·13273; 0·13302; 0·13421. Mean, 0·1331.

The ratios between the middle quantity and the smallest quantity were also determined:—

Ratios.—0·09224; 0·09238; 0·09285; 0·09290; 0·09222. Mean, 0·09252.

Ratio between smallest and largest quantities, 0·0132.

Since the weight of the largest quantity is calculated from its specific gravity, and the ratio between that and the smallest is known, that of the smallest also depends on the relative proportions of alcohol and ether. It may be confidently assumed that all three portions have the same composition; for, in order to obtain the middle quantity, the tube was inverted after thorough mixture had been ensured, and a portion of the mixed liquid allowed to escape through the mercury; and the smallest quantity was obtained in a similar manner.

We have now two means of calculating the weights of the smallest quantity for different molecular proportions; first from the normal vapour-density, by the method already described; and, second, from the specific gravities of the liquid, also calculated for different molecular proportions.

The results of the first process are as follows, where x is the number of molecules of alcohol in 100 of the mixture:—

	Vapour-density.	Weight.	Vol. of 1 gram liquid at 0°.	Weight.
x = 50......	30·0	0·003566	1·3036	0·003312
55......	29·3	0·003483	1·2979	0·003326
60......	28·6	0·003400	1·2920	0·003342
65......	27·9	0·003316	1·2857	0·003358
70......	27·2	0·003233	1·2791	0·003375

On mapping the weights obtained by both methods against values of x, the point of intersection of the two curves gives the value of x as 63, and of the weight as 0·003352 gram, and the volume of 1 gram of the mixed liquid at 0° is consequently 1·2882 c.c.

From the ratios previously stated it follows that the weight of the middle quantity is 0·03623 gram, and that of the largest, 0·27204 gram.

Similar comparisons of the smallest quantities among themselves gave the weight of that portion used for the isothermals 160°, 0·003313 gram, and for the isothermals 250° and 275°, 0·003479 gram.

REDUCTION AND ARRANGEMENTS OF RESULTS.

Vapour-pressures.

It has already been pointed out that the vapour-pressures of a mixture vary with the volume, and that pressure continues to rise, on diminution of volume, even after liquid has begun to appear. For example, at 190° liquid begins to be visible at a pressure of 22000 mm , and the last bubble of gas disappears at about 24600 mm. The pressure has thus risen 2600 mm., or over 10 per cent. of its total amount during condensation. The rise of pressure is even more remarkable at lower temperatures. At 80°, condensation begins at a pressure of about 1200 mm., and the last trace of gas is condensed at 2290 mm. The pressure is therefore nearly doubled during condensation. It is clear from this that any attempt (and attempts have been made) to determine the vapour-pressure of a mixture by the statical method must lead to wholly erroneous, and indeed uninterpretable results, inasmuch as the relative quantities of the two substances in the residual liquid would alter with each alteration of volume. Moreover, by the dynamical method, the results can only be even approximately correct when the volume of liquid is very large compared with the volume of vapour.

Compressibilities of Liquid.

The isothermals for the liquid state, showing decrease of volume on increase of pressure, were for purposes of smoothing mapped on curve-paper, and isobars were drawn representing the relations of volume to temperature. The isothermals are shown on Plate I. The circles on the diagram are the experimental points; the crosses are retransferred from the isochors.

The results are given in the table (p. 772).

Orthobaric Volumes of 1 *gram of Liquid.*

Temp.	Volume.	Temp.	Volume.	Temp.	Volume.
0°	1·288	80°	1·4365	150°	1·6785
10	1·302	90	1·461	160	1·733
20	1·3195	100	1·489	170	1·7965
30	1·3365	110	1·520	180	1·874
40	1·354	120	1·552	190	1·976
50	1·373	130	1·590	200	2·107
60	1·393	140	1·6305	210	2·327
70	1·413				

Pressure in Millimetres.

T.	1500.	5000.	10000.	15000.	20000.	25000.	30000.	35000.	40000.	42500.	45000.	47500.	50000.	55000.
20°	1·320	1·319	1·318	1·317	1·316	1·314	1·313	1·312	1·311	1·311	1·311	1·310	1·310	1·310
30	1·336	1·335	1·334	1·332	1·331	1·330	1·3285	1·327	1·3265	1·326	1·3255	1·325	1·324	1·3235
40	1·354	1·352	1·351	1·3495	1·348	1·3465	1·345	1·3435	1·3425	1·342	1·341	1·340	1·3395	1·3385
50	1·3725	1·371	1·369	1·368	1·366	1·364	1·362	1·361	1·360	1·359	1·358	1·357	1·356	1·3545
60	1·393	1·3915	1·389	1·387	1·3855	1·3835	1·381	1·380	1·3785	1·378	1·3765	1·3755	1·374	1·372
70	1·416	1·413	1·410	1·408	1·406	1·402	1·4015	1·400	1·398	1·397	1·396	1·395	1·3935	1·3915
80	—	1·436	1·433	1·4305	1·428	1·426	1·4235	1·421	1·420	1·418	1·417	1·416	1·414	1·412
90	—	1·462	1·458	1·4555	1·452	1·4495	1·447	1·4445	1·4425	1·441	1·440	1·4385	1·437	1·434
100	—	1·4895	1·4855	1·482	1·4785	1·4755	1·4725	1·470	1·468	1·466	1·465	1·4635	1·4615	1·459
110	—	1·520	1·516	1·5115	1·508	1·504	1·501	1·4985	1·496	1 494	1·492	1·490	1·488	1·485
120	—	—	1·5495	1·545	1·5405	1·536	1·5325	1·530	1·526	1·524	1·522	1·520	1·517	1·514
130	—	—	1·5875	1·582	1·5775	1·571	1·5675	1·564	1·559	1·5565	1·554	1·552	1·549	1·545
140	—	—	1·631	1·624	1·6195	1·6115	1·606	1·6015	1·596	1·593	1·590	1·588	1·585	1 580
150	—	—	—	1·672	1·666	1·658	1·6505	1·6445	1·638	1·634	1·631	1·6285	1·624	1·619
160	—	—	—	1·732	1·723	1·712	1·7025	1·694	1·685	1·6815	1·678	1·674	1·670	1 6635
170	—	—	—	—	1·792	1·778	1·765	1·752	1·741	1·735	1·732	1·729	1·724	1·715
180	—	—	—	—	—	1·860	1·840	1·826	1·810	1·803	1·7965	1·7905	1·784	1·771
190	—	—	—	—	—	1·980	1·949	1·920	1·8965	1·888	1·878	1·869	1 860	1·841
200	—	—	—	—	—	—	—	2·055	2·014	1·996	1·980	1·967	1·954	1.938
210	—	—	—	—	—	—	—	2·305	2·193	2·157	2·128	2·101	2·080	2·051
220	—	—	—	—	—	—	—	—	2·775	2·516	2·405	2·334	2·283	2·210
230	—	—	—	—	—	—	—	—	—	—	—	2·960	2·711	2·444

These numbers are calculated from volumes directly read after the last trace of vapour had disappeared at the top of the experimental tube. It is questionable whether the word "orthobaric" should be used; but by the method of measurement, the true vapour-pressure of the mixture must have been nearly obtained. The volumes were plotted against temperature, smoothed graphically, and reproduced as above.

Inasmuch as it is impossible to detect the volume at which the first trace of liquid makes its appearance in the experimental tube, it is impossible to give the volumes of the saturated vapour. These numbers cannot be read from the curves, for the transition from gas to liquid is accompanied by gradual rise of pressure; there is no definite angle between the line representing volumes in the gaseous condition, and that representing the state in which liquid and gas are both present at once. For the same reason, it is impossible to calculate the heats of vaporisation.

Two points of interest present themselves. In the case of pure stable liquids, the isochoric lines, or lines of equal volume, are straight, both for the liquid and the gaseous states. It is an interesting question whether the isochoric lines of a mixture are similar to those of a pure substance, or whether they are sinuous curves, in some way resembling those of a dissociable body (see *Phil. Mag.*, 1887, May and July). Another question is, what alteration occurs in the volumes of the two liquids or gases on mixing? How do the volumes of the mixture compare with the sums of the volumes of the constituents? We shall consider these points in their order.

Isochoric Lines.

The isochors for the liquid state were constructed from the isobars; they are represented on Plate III. From this it will be seen that from volumes of 1·32 c.c. per gram up to 2·7 c.c. per gram, the isochoric lines are straight between wide limits of pressure. As the volumes increase, the isochors, which were constructed from the isotherms, begin to show curvature which increases with rise of volume; and the curvature of each individual isochor increases with fall of pressure and temperature. This is evident on the diagram at volumes between 9 c.c. per gram and 30 c.c. per gram. It is probable that if measurements could have been made at still higher temperatures, these lines would also have become straight. Towards 30 c.c. per gram, the isochors are again becoming straighter, and at still larger volumes deviation from straightness becomes imperceptible at high temperatures. It is to be noticed, however, that at lower temperatures, these isochors exhibit curvature on approaching the vapour-pressure *band.*

It has been already remarked that the pressure of the vapours of a mixture of liquids depends on their relative amounts, which again depends on the relative volumes of the liquid and vapour. As these are continually changing during evaporation, the vapour-pressures are representable not by a line but by a band. This is well seen in the diagram of isochoric lines (Plate III); and, as has been remarked, the isochors show curvature before reaching this band, whereas with a pure liquid the isochors remain perfectly straight, and indeed can be induced to cut the vapour-pressure line. This curvature of the isochoric lines appears to be sudden for small volumes (liquid), but is gradual at large volumes (gas).

It is a question of interest whether such isochoric lines for a mixture of liquids can be conceived to cut through the vapour-pressure band. It may be remembered that in the case of pure liquids this is experimentally possible. In order that it may be experimentally realised it is necessary to work with liquid almost absolutely free from air; and our test, applicable in the case of pure liquids, was the absolute constancy of vapour-pressure through the whole process of condensation. But with a mixture this test is clearly inapplicable; and the only test which we have to rely on is to notice whether or not the pressure rises greatly during the condensation of the last small bubble of gas. So far as we could judge, this test gave fairly satisfactory results; when the liquids were mixed, the small bubble disappeared quickly. But it was found impossible to reduce pressure to any great extent without the bubble again appearing. It may have been the case, therefore, that a little air was present, preventing the partial realisation of the continuous passage from liquid to gas.*

Alteration of Volume on Mixing.

The second point of interest is as regards the alteration of volume on mixing alcohol and ether at any given temperature and pressure. From previous experiments, we know the volume of 1 gram of alcohol and also the volume of 1 gram of ether at any given temperature and pressure; and we also know the proportion of alcohol to ether in the mixture. The volume of the alcohol, supposing it to be unmixed, will clearly be proportional to its weight in a gram of the mixture, and similarly with ether. For purposes of comparison, three isobars were constructed, one for alcohol, one for ether, and one for the mixture; and from these isobars the volumes corresponding to particular temperatures were read off. The volumes of alcohol and ether were then reduced so as to be proportional to their relative weights in the mixture. For example, at a pressure of 40000 mm., and at a temperature of 190°, the volume of 1 gram of ether is 2·211 c.c.; and that of 1 gram of alcohol is 1·690 c.c. The volume of 0·4858 gram of ether is therefore 1·074 c.c., and of 0·5142 gram of alcohol 0·8690 c.c. The sum of these is 1·943 c.c., while the volume of 1 gram of the mixture at the same pressure and temperature is 1·897 c.c. The actual contraction is 0·046 c.c., and the percentage contraction on mixing is 2·37 per cent.

---

* From this it is evident that Wroblewski's conclusion (*Monats. f. Chem.*, 1886, p. 383) regarding a pure liquid is realisable only in the case of a mixture, viz., that the isochoric lines, after approaching the vapour-pressure line, run parallel with it.

Three pressures were chosen: the first, 50000 mms., is above the critical pressure of all; the second, 40000 mms., is above the critical pressure of ether and of the mixture, but below that of alcohol; and the third, 5000 mms., is below that of all. The comparisons in the first case are all from experimental data; they are given in the following table, and are graphically represented on Plate IV.

Temperature.	Vol. of 0·4858 gram of ether.	Vol. of 0·5142 gram of alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
	c.c.	c.c.	c.c.		
150	0·8793	0·7739	1·6532	1·624	−1·77
170	0·9352	0·8124	1·7476	1·724	−1·35
190	1·0226	0·8639	1·8865	1·860	−1·40
200	1·0858	0·8947	1·9805	1·954	−1·34
210	1·1708	0·9281	2·0989	2·080	−0·90
220	1·2850	0·9770	2·2620	2·283	+0·93
230	1·4501	1·0515	2·5016	2·710	8·33
234	1·559	1·098	2·657	3·150	18·55
236	1·584	1·126	2·710	3·505	29·34
238	1·627	1·157	2·784	3·950	41·88
240	1·681	1·201	2·882	4·410	53·01
242	1·732	1·260	2·992	4·785	59·93
244	1·790	1·365	3·155	5·100	61·65
246	1·846	2·139	3·985	5·400	35·51
248	1·904	2·915	4·819	5·675	17·76
250	1·972	3·330	5·302	5·930	11·85
255	2·138	4·011	6·149	6·490	5·55
260	2·283	4·522	6·805	6·965	2·35
270	2·536	5·265	7·801	7·740	−0·78
275	2·655	5·574	8·229	8·040	−2·30

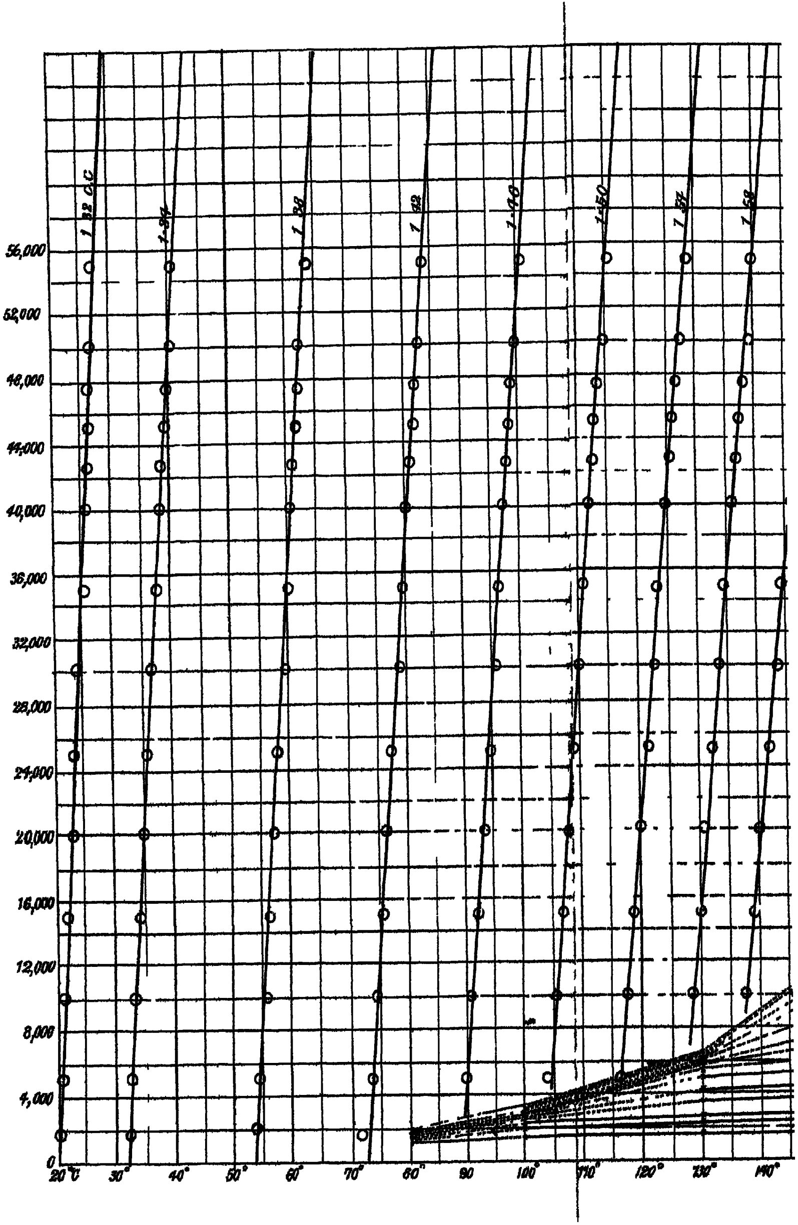
The pressure of 40000 mm. is below the critical pressure of alcohol. A portion of the isobar, therefore, takes the serpentine form characteristic of the continuous passage from the liquid to the gaseous state; and between the temperatures 231° and 236° there are for each temperature three possible volumes, two of which are realisable at the boiling point corresponding to that pressure, but only one at any other temperature. The isobar, however, was constructed from the known values of *a* and *b* for alcohol in the quation $p = bt - a$, and the required volumes were read from its graphic representation. The following table summarises the results, which are also shown graphically in Plate IV:—

Temperature.	Vol. of 0 4858 gram of ether.	Vol of 0·5142 gram alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
°	c c.	c.c.	c.c.		
100	0·7768	0 7091	1·4859	1·468	− 1·20
120	0·8123	0·7307	1·5430	1·526	− 1·10
140	0·8589	0·7600	1·6189	1·596	− 1·41
160	0 9206	0 7955	1·7161	1·686	− 1·75
180	1·0085	0·8412	1·8497	1·810	− 2·14
190	1·074	0·8690	1·9430	1·897	− 2·37
200	1·170	0·9024	2·0724	2·014	− 2·82
210	1·341	0·9430	2·2840	2·193	− 3·98
215	1·478	0·968	2·446	2·350	− 3·90
218	1·603	0·986	2 589	2·559	− 1·16
220	1·700	1·001	2·701	2 776	+ 2·78
222	1·777	1·017	2·794	4 795	+ 71 62
223	1·807	1·026	2·833	5·380	+ 89·87
230	2 220	1·112	3·332	7·120	+113·74
231	2 274	3·466	5·740	7·300	+ 27·18
„	„	2·890	5·164	„	+ 41·36
„	„	1·131	3·405	„	+114 39
232	2·322	3·913	6·235	7·440	+ 19·32
„	„	2 509	4·831	„	+ 54·00
„	„	1·144	3·466	„	+114·66
233	2·371	4·196	6·567	7·600	+ 15·73
„	„	2·247	4·618	„	+ 64 57
„	„	1·170	3·541	„	+114·63
234	2·414	4·412	6·826	7·740	+ 13·39
„	„	2·026	4 440	„	+ 74·32
„	„	1·193	3·607	„	+111·58
235	2·461	4·582	7·043	7·900	+ 12·17
„	„	1·846	4·307	„	+ 83 42
„	„	1·229	3·690	„	+114·10
236	2·507	4·716	7·253	8·010	+ 10·44
„	„	1·635	4·112	„	+ 93·39
„	„	1·280	3·787	„	+111·51
237	2·550	4·890	7·410	8·140	+ 9·41
210	2·677	5·281	7 958	8·510	+ 6·94
250	3·041	6·278	9·319	9·550	+ 2·48
275	3·789	7·610	11·399	11 400	0

As we have been unable to discover a formula representing the behaviour of the mixture, we are precluded from giving results at a low pressure in the unrealisable portion of the passage from gas to liquid, if indeed it is conceivable in the case of a mixture. We have therefore calculated only the gaseous portions at a pressure of 5000 mm. We append the results:—

Journ Chem Soc October 1887.

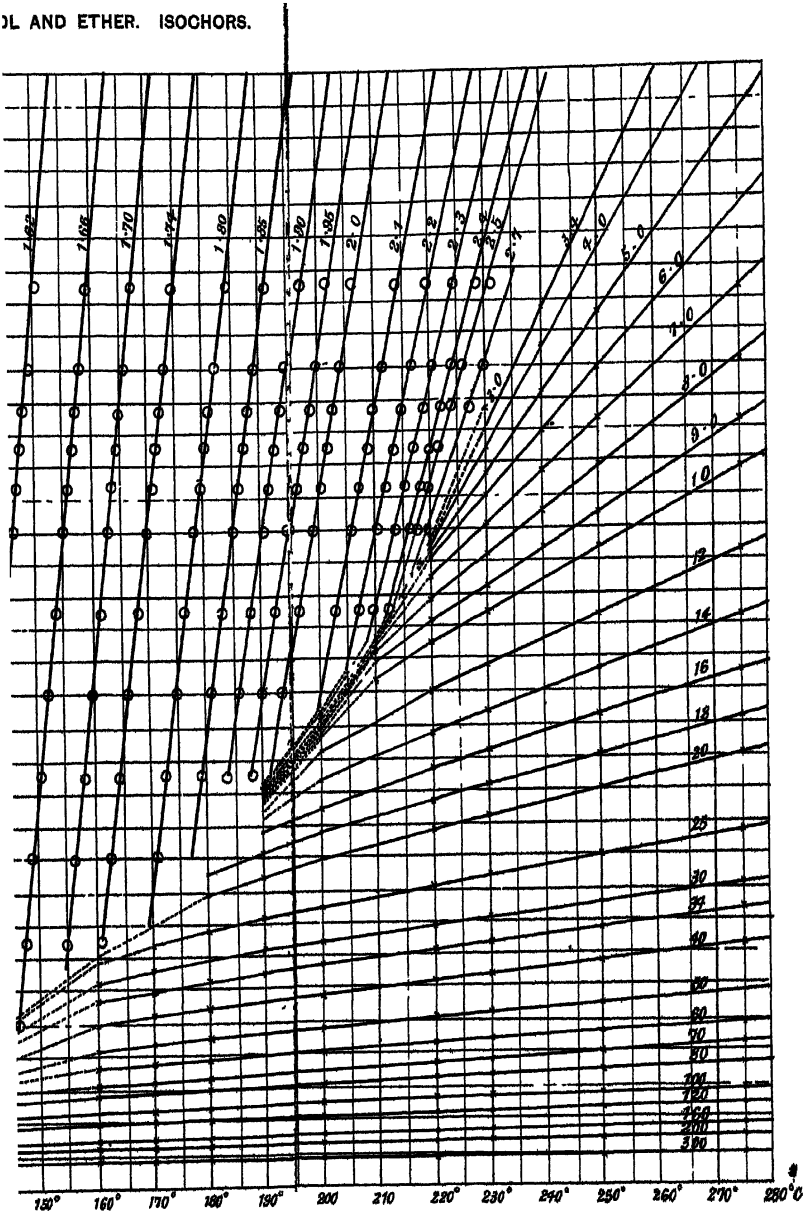
MIXTURE OF ALCOH



Harrison & Sons

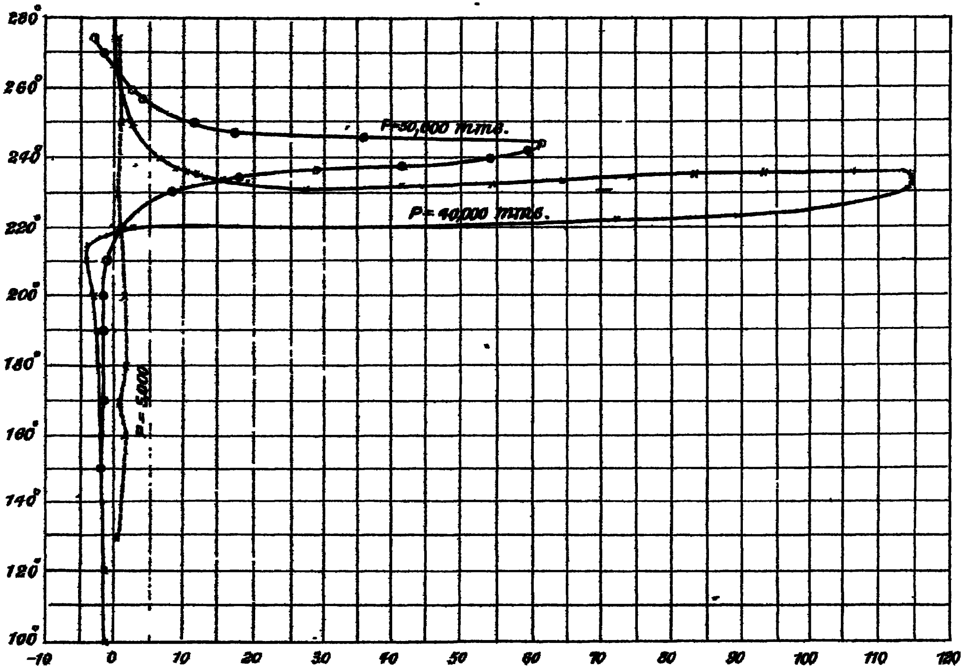
RAMSAY & YOUNG.
Plate 3

)L AND ETHER. ISOCHORS.



Lith St Martins Lane W C

PRESSURES AND TEMPERATURES.



Harrison & Sons, Lith. St Martins Lane, W C

Temperature.	Vol. of 0 4858 gram of ether.	Vol. of 0·5142 gram alcohol.	Sum.	Vol. of 1 gram of mixture.	Percentage alteration.
°	c.c.	c.c.	c c.		
130	28·69	50·55	79·24	79·3	+0·76
160	31·72	56·46	88·18	90·0	2·06
170	32·74	58·36	91·10	92·1	1·10
180	33·85	60·12	93·97	95·7	1·84
200	35·80	63·81	99·61	101·1	1·50
220	37·75	67·36	105·11	105·9	0·75
230	38·72	69·06	107·78	108·1	0·30
250	40·54	72·50	113·04	114·1	0·94
275	42·85	76·72	119·57	120·2	0·53

It may appear remarkable that on mixing two bodies at the same pressure and temperature, a great expansion should be produced. But a familiar and somewhat analogous instance is at hand. Imagine a litre of dry air at a given temperature and pressure. Let a drop of liquid water be introduced; the sum of the volumes does not differ appreciably from 1 litre. But the water will evaporate into the dry air, and the volume of the "mixture" will be considerably greater than the sum of the volumes of the "constituents." The greatest expansion, at 232° under a pressure of 40000 mm., occurs precisely in this manner; the liquid alcohol is gasified by expansion into the space occupied by the ether. Above the critical pressure of alcohol at 50000 mm., a similar, though not so great, expansion is noticeable, even if the alcohol cannot be termed a "liquid."

DESCRIPTION OF PLATES.

Plate I shows the compressibilities of the liquid. The circles represent actual observations with the largest quantity of substance. The crossed circles show the effect of incomplete mixture, with the exception of those marked E. The crosses are points read from the isochors, on the apparently well-grounded assumption that in this region the isochors are straight lines.

Plate II represents the experiments with the middle quantity. The circles trace out the isotherms. The crossed circles represent observations with either the largest or the smallest quantity, the former at small volumes, the latter at large. The lines radiating from the vapour-pressure band are isochors for volumes between 2 c.c. per gram and 34 c.c. per gram. The vapour-pressure band is shown by the dotted lines.

Plate III gives the isochors, from volumes of 1·32 to 300 c.c. per gram. The general course of the vapour-pressure band is here well seen.

Plate IV represents the percentage alteration of volume on mixing the alcohol and ether at constant temperature and pressure. The lines are isobars for 5000, 40000, and 50000 mm.

LXXVIII.—*The Compounds of Ethyl Alcohol with Water.*

By D. Mendeléeff.

Dalton's great doctrine respecting the atomic constitution of matter has not hitherto been applied to the explanation of the phenomena of dissolution, and notwithstanding the many admirable investigations on this subject, the views of chemists respecting the relation between ordinary cases of combination and the phenomena of dissolution remain still undefined. However, the part played by solutions in nature, in the laboratory, and in the arts, is so important that the fulness of our chemical conceptions seems to suffer from the want of clearness in the doctrine relating to them.

In communicating the result of some of my investigations and hypotheses, I will restrict myself to the particular case of solutions of ethylic alcohol in water, chiefly because, among solutions, the mixtures of alcohol and water have been most fully studied, at any rate, with reference to the dependence of change of specific gravity on the proportion of alcohol. Practical necessity has led to many accurate investigations of this subject, and from the time of Gilpin to our own the mass of accurate information has been steadily increasing, and permits of a sound judgment being formed. Collating all the information at our disposal, I have constructed the following Table (I) of the most trustworthy data :—

Table I.

Percentage by weight of alcohol, *p*.	Specific gravity in a vacuum at 15° C., taking water at 4° = 10,000, and at 15° = 9991·6, *s*.	Percentage by weight of alcohol, *p*.	Specific gravity in a vacuum at 15° C., taking water at 4° = 10,000, and at 15° = 9991·6, *s*.
5	9904·1	55	9067·4
10	9831·2	60	8953·8
15	9768·4	65	8838·6
20	9707·9	70	8719·5
25	9644·3	75	8601·4
30	9570·2	80	8479·8
35	9484·5	85	8354·8
40	9389·6	90	8225·0
45	9287·8	95	8086·9
50	9179·0	100	7936·6

It is interesting to note that, after making some necessary corrections, the data mentioned by different observers, taking only the most trustworthy observations, show very small differences. For example, in the case of a solution of 50 per cent. of alcohol we find the following :—

TABLE II.

Gilpin	1792	9187·0
Gay-Lussac	1824	9182·0
Fownes	1847	9180·0
Drinkwater	1848	9178·8
Baumhauer	1860	9180·0
Mendeléeff	1865	9179·7
Dupré and Page	1869	9178·5
Squibb	1884	9178·0

In the above table of specific gravities, the greatest error is within 0·0002, and only in some cases attains 0·0003. No other solution besides that of alcohol, and none of its other properties, are known with such a degree of accuracy, and in addition the solutions can be obtained in all proportions, and therefore the example which I have taken is a typical one.

Without describing the methods by which I have arrived at my views on the nature of solutions (some of the preliminary investigations on this subject have been published by me in the *Journal of the Russian Chemical Society*, and in Professor Ostwald's *Zeitschrift für physikalishe Chemie*), I will now state the hypothesis which is in accordance with them.

Solutions may be regarded as strictly definite, atomic chemical combinations at temperatures higher than their dissociation temperature. Definite chemical substances may be either formed or decomposed at temperatures which are higher than those at which dissociation commences; the same phenomenon occurs in solutions; at ordinary temperatures they can be either formed or decomposed. In addition, the equilibrium between the quantity of the definite compound and of its products of dissociation is defined by the laws of chemical equilibrium, which laws require a relation between equal volumes and their dependence on the mass of the active component parts. Therefore, if the above hypothesis of solution be correct, comparisons must be made of equal volumes; the specific gravities are the weights of equal volumes, and moreover we must expect the specific gravities of solutions to depend on the extent to which the active substances are produced; therefore, the expression for specific gravity s, as a function of the percentage composition p, must be a parabola of the second order :—

$$s = N(p \pm a)(100 - p \mp a),$$

or this may be represented by the general equation—

$$s = C + Ap + Bp^2.$$

Between two definite compounds which exist in solutions, we must expect that the differential coefficient $\frac{ds}{dp}$ will be a rectilinear function of p:

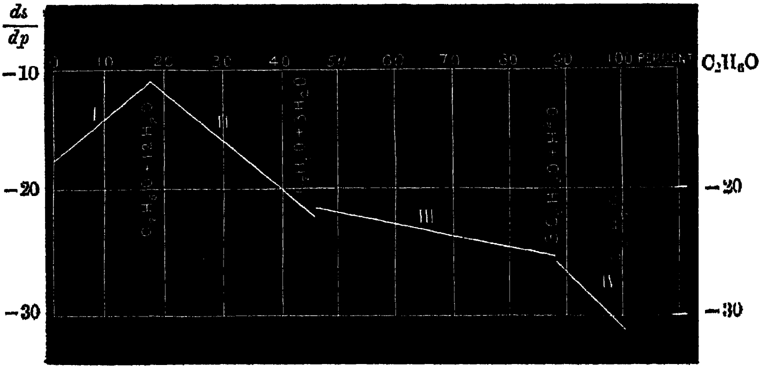
$$\frac{ds}{dp} = A + 2Bp.$$

This consequence can, in the first place, be verified by experiment, and secondly gives the means of ascertaining what are the definite combinations existing in the solution.

Applying this method to the solution of H_2O and C_2H_6O, three definite combinations are found to exist, namely—

$$\begin{array}{rcl} C_2H_6O + 12H_2O & = & 17{\cdot}56 \text{ per cent. alcohol.} \\ C_2H_6O + 3H_2O & = & 46{\cdot}00 \quad\text{,,}\quad\text{,,} \\ 3C_2H_6O + H_2O & = & 88{\cdot}46 \quad\text{,,}\quad\text{,,} \end{array}$$

The rectilinear character of the differential coefficient $\frac{ds}{dp}$ is demonstrated by the annexed diagram:—



The parabolas expressing the specific gravities at 15° C. are calculated by the formulæ—

$$\begin{array}{lrl} \text{I.} & s = & 9991{\cdot}6 - 17{\cdot}99p + 0{\cdot}1958p^2 \\ \text{II.} & s = & 9868{\cdot}4 - 4{\cdot}0975p - 0{\cdot}1958p^2 \\ \text{III.} & s = & 10166{\cdot}6 - 17{\cdot}545p - 0{\cdot}0443p^2 \\ \text{IV.} & s = & 9074{\cdot}9 + 8{\cdot}192p - 0{\cdot}1958p^2 \end{array} \left\{\begin{array}{l} 9991{\cdot}6 \\ 9736{\cdot}1 \\ 9265{\cdot}6 \\ 8267{\cdot}4 \\ 7936{\cdot}1 \end{array}\right. .$$

With change of temperature, the constants of the parabola change, but for temperatures between −30° and +40°, at which accurate observations exist, the applicability of the parabolic expression is as exact as it is at 15°, and for that temperature an example is given in line III, which is the longest traced. The difference between the calculated and the observed results in no case exceeds the allowable errors of experiment, as the following table shows:—

TABLE III.

Percentage of alcohol.	Value by experiment. Specific gravity.	Value by calculation. Specific gravity.
50	9179·0	9178·4
55	9067·4	9067·3
60	8953·8	8954·1
65	8838·6	8838·6
70	8719·5	8721·0
75	8601·4	8601·1
80	8479·8	8479·0
85	8354·8	8354·7

The hypothesis respecting the rectilinear character of the differential coefficient $\frac{ds}{dp}$ has been proved to be correct, not only for solutions of a hundred different salts, but also for solutions of H_2SO_4, of NH_3, of HCl, and other similar substances, and up to this time I have not met with a single solution which is an exception.

As the principle of my hypothesis lies in the idea of dissociation of definite compounds which exist in solutions, I intend to investigate minutely solutions at low temperatures, and I expect to obtain definite compounds in the solid state, and to explain the relation of the solid compounds which were obtained by me in 1868, and afterwards by Guthrie, who called them cryohydrates; indeed I have already made some experiments in that direction with the assistance of Mr. Tooshenko. Thus we have obtained the definite compound $C_2H_6O + 12H_2O$ in the solid state at −17° C., and the definite compound $C_2H_6O + 3H_2O$ in the crystalline form, at a temperature which is attained by the mixture of solid carbonic anhydride and ether.

The fundamental propositions of my investigations, that is to say, firstly, the rectilinear character of the differential coefficient $\frac{ds}{dp}$; and, secondly, the existence in solutions of definite combinations, I am developing in a special paper, in which I attempt, as far as possible, to distinguish clearly that portion of the theory which does not admit of question from the hypothesis which still requires verification and amplification.

I do not consider that my investigations are finally completed, and I only venture to lay them before a scientific society as footsteps along the road leading to the elucidation of the theory of dissolution in the light of Dalton's teaching, and with the help of modern views respecting dissociation and the dynamic equilibrium of molecules, which I may be allowed to term "association."

LXXIX.—*Isomeric Change in the Phenol Series.* (Second Notice.)

By Arthur R. Ling.

In extending the experiments recorded in my previous communication on "The Action of Bromine on the Dibromonitrophenols" (this vol., p. 147), to some other nitro-halogen-derivatives of phenol, I have obtained results which are, I think, sufficiently interesting for publication.

II. *The Action of Bromine on the Dichloronitrophenols.*

1. *Dichlororthonitrophenol.*—This compound was prepared in two ways, viz., by chlorinating orthonitrophenol, and by nitrating crude dichlorophenol, the product in each case being purified by means of the potassium salt, which crystallises from water in anhydrous flat red needles or plates. The following result of a potassium determination shows that the substance was pure:—

0·3148 gram dried at 100° gave 0·1130 gram K_2SO_4.

	Theory. $C_6H_2Cl_2NO_3K$.	Found.
K........	15·87 per cent.	15·75 per cent.

On treatment with dilute hydrochloric acid, this salt yielded dichlororthonitrophenol, crystallising from alcohol in light yellow plates melting at 123°, the recorded melting point. 10 grams of dichlororthonitrophenol was placed in a bottle together with one molecular proportion of bromine (8 grams), and about 40 c.c. of water; the stopper being fastened down with copper wire, the bottle was heated in a bath of boiling water for several hours. The bromine was entirely absorbed, and oxides of nitrogen escaped on releasing the stopper The product was washed with water, dried and boiled with alcohol which dissolved the greater portion. The residue was found to consist of a substance which dissolved but sparingly in alcohol, was insoluble in potassium carbonate solution, and did not contain nitrogen. In a second experiment similarly conducted, after a preliminary exhaustion with alcohol, the residue was dried and treated with benzene, in which it was found to be easily soluble, and to be deposited from the hot solution in glistening yellow plates, much resembling bromanil in appearance. A further qualitative examination showed that it contained both chlorine and bromine.

The portion dissolved by alcohol in the two foregoing experiments consisted of unaltered dichloronitro-compound. It seemed desirable, however, to obtain a larger quantity of the chlorobromo-derivative before investigating any other products of the reaction.

Since the reaction between dichlororthonitrophenol and bromine appeared somewhat analogous to that between dibromorthonitrophenol and bromine, it was probable that the unknown compound was a tetra-substitution-derivative of quinone, and if such were the case, it might be, assuming the parachlorine-atom in dichlororthonitrophenol, after its first displacement, to be rendered active by the nitric acid resulting from the displacement of the NO_2-group, a dichlorodibromoquinone, two of which are known; or, if otherwise it might be chlorotribromoquinone, a hitherto unknown compound. Analysis has shown it to be the latter.

Chlorotribromoquinone.—In order to prepare this compound in larger quantity, several quantities of 5 grams of dichlororthonitrophenol were heated as before described with bromine in the proportion $C_6H_3Cl_2NO_3 : 4Br_2$ and water. The reaction takes place so readily that chlorotribromoquinone may be prepared by merely heating the dichloronitro-compound on the water-bath with bromine and water, in a flask connected with a reflux condenser. After the usual preliminary purification, the compound was crystallised from benzene. A certain portion was recrystallised from glacial acetic acid.

The numbers obtained on analysis were as follows:—

I. 0 1983 gram dried at 100° gave 0·1405 gram CO_2.
II. 0·2067 „ „ 0·3860 „ $AgCl(AgBr)_3$.
III. 0·3392 „ „ 0·6328 „ $AgCl(AgBr)_3$.

	Theory. $C_6ClBr_3O_2$.	Found. I.	Found. II.	Found. III.	
C	18·97 per cent.	19·31	—	—	per cent.
*Cl ... Br ...	72·59 „	—	72·85	72·78	„

---

* So many halogen determinations have been made of this compound and its

The equation showing the formation of chlorotribromoquinone from dichlororthonitrophenol and bromine is therefore—

$$C_6H_2Cl_2(NO_2)\cdot OH + 4Br_2 + 2H_2O = C_6ClBr_3O_2 + 5HBr + HCl + HNO_3.$$

Chlorotribromoquinol.—5 grams chlorotribromoquinone was introduced into a flask together with a solution of stannous chloride; the flask was connected with a reflux condenser, and the solution boiled on a sand-bath for about 20 minutes. The substance had then lost its yellow colour. It was thrown on to a filter, washed with water, and crystallised from benzene, from which it separated in colourless needles. After recrystallisation, the melting point was found to be 234°.

A specimen dried at 100° gave the following result on analysis:—

0·2920 gram gave 0·5411 $AgCl(AgBr)_3$.

	Theory. $C_6ClBr_3(OH)_2$.	Found.
Cl Br	72·21 per cent.	72·26 per cent.

Diacetylchlorotribromoquinol.—To prepare this compound, 2 grams chlorotribromoquinol was boiled with acetic anhydride for about two hours in a flask attached to a reflux condenser. It crystallises from benzene in colourless microscopic prisms, melting at 262°.

0·1950 gram dried at 100° gave 0·2953 gram $AgCl(AgBr)_3$.

	Theory. $C_{10}H_4ClBr_3O_4$.	Found.
Cl Br	59·18 per cent.	59·08 per cent.

Chlorobromanilic Acid.—When chlorotribromoquinone is treated with potash according to Stenhouse's method, the potassium salt of chlorobromanilic acid (dihydroxychlorobromoquinone) is obtained. On adding an acid to an aqueous solution of the salt, the hydroxy-derivative is obtained. Chlorobromanilic acid was first described by Krause (*Ber.*, 12, 47), who prepared its potassium salt by the action of potash on metadichlorometadibromoquinone.

It is not at all easy to decompose chlorotribromoquinone with potash at the ordinary temperature; for example, 5 grams was not entirely decomposed in a week, although the flask containing the mixture was shaken vigorously at intervals during each day. If,

---

derivatives, and the numbers so closely approximate those demanded by theory, that I did not separate the chlorine and bromine. The silver precipitate has, however, in each experiment been qualitatively examined.

however, the solution be heated to boiling, the transformation takes place at once, but the yield is very considerably diminished. It has been found best to perform this experiment at 70—80°; the reaction is then complete in about six hours if 5 grams of substance be used. In no case is anything like the theoretical yield obtained; the largest quantity of the pure chlorobromanilic acid obtained from 5 grams of chlorotribromoquinone was under 1 gram.

A specimen recrystallised from water, and dried at 100°, was analysed with the following result:—

0·1962 gram gave 0·2541 gram $AgCl(AgBr)_3$.

	Theory. $C_6ClBrH_2O_4$.	Found.
Cl Br	45·56 per cent.	45·21 per cent.

Potassium Chlorobromanilate.—Some of the chlorobromanilic acid was converted into the potassium salt by means of potassium carbonate. The resulting salt recrystallised from water and dried between filter-paper was then analysed.

I. 0·2259 gram lost 0·0227 gram at 100—120°.
II. 0·3537 gram gave 0·1849 gram K_2SO_4.

	Theory. $C_6ClBrK_2O_4 2,OH_2$.	Found. I.	 II.	
H_2O	9·84 per cent.	10·04	—	per cent.
K	21·34 ,,	—	21·45	,,

0·2007 gram anhydrous salt gave 0·1063 gram K_2SO_4.

	Theory. $C_6ClBrK_2O_4$.	Found.
K	23·67 per cent.	23·71 per cent.

Several experiments were made in order to ascertain whether, when dichlororthonitrophenol is heated with water and an insufficient quantity of bromine to entirely convert it into chlorotribromoquinone, the residual dichloronitro-compound undergoes isomeric transformation or any other change, the quantities used being 10 grams of dichlororthonitrophenol to 1 molecular proportion bromine and about 40 c.c. water. The heating was continued for several days, and the products, after washing, were boiled with potassium carbonate solution. The quinone-derivative was, in each case, decomposed by this treatment. In one instance, it appeared as a black carbonaceous mass, and in all the others as an amorphous, earth-coloured powder, which dissolved easily in benzene, but from which nothing definite could be obtained.

The action of alkalis, and more especially of carbonated alkalis, on tetra-halogen-derivatives of quinone is, in my opinion, worthy of attention. Stenhouse mentions, in describing the preparation of chloranilic acid from chloranil (*Jour. Chem. Soc.*, 1870, 6), that, although potassium chloranilate was produced by the action of potassium carbonate on chloranil, a much better yield was obtained when caustic potash was used.

The alkaline extract from these experiments was found to consist of the potassium-derivative of dichlororthonitrophenol, and hence it may be satisfactorily concluded that this compound undergoes no change when treated in the manner above mentioned. A specimen of the salt was recrystallised and analysed.

0·1503 gram dried at 100° gave 0·0529 gram K_2SO_4.

	Theory $C_6H_2Cl_2NO_3K$.	Found.
K	15·87 per cent.	15 76 per cent.

A portion treated with dilute hydrochloric acid and crystallised from alcohol was found to melt at 123°.

2. *Dichloroparanitrophenol.*—This was prepared by chlorinating paranitrophenol and purified by means of the potassium or barium salt. A barium salt has been obtained which agrees in appearance with one described in the text-books as crystallising in red needles containing 4 mols. H_2O. The salt obtained, however, apparently only contains $3\frac{1}{2}$ mols. H_2O. The following is the result of analysis:—

0·2838 gram lost 0·0290 gram at 100—120° and gave 0·1077 gram $BaSO_4$.

	Theory. $(C_6H_2Cl_2NO_3)_2Ba,3\frac{1}{2}H_2O$.	Found.
H_2O	10·26 per cent.	10·21 per cent.
Ba..........	22·31 ,,	22·31 ,,

10 grams of dichloroparanitrophenol was heated in the usual manner with bromine and water, the proportions used being

$$C_6H_3Cl_2NO_3 : 4Br_2.$$

The product was crystallised from glacial acetic acid, and had the general form of the tetra-halogen-derivatives of quinone, viz., golden-yellow laminæ. A specimen dried at 100° was then analysed.

0·1916 gram gave 0·3787 gram of a mixture of AgCl and AgBr, which on complete reduction gave 0·2469 gram metallic silver = 0·1662 gram AgCl and 0·2125 gram AgBr.

	Theory. $C_6Cl_2Br_2O_2$.	Found.
Cl..........	21·19 per cent.	21·50 per cent.
Br..........	47·76 ,,	47·29 ,,

The compound was therefore a dichlorodibromoquinone, and as it was obtained from dichloroparanitrophenol, it must be the metadichlorometadibromoquinone described by Krause (*Ber.*, **12**, 47).

2 grams metadichlorometadibromoquinone was treated with potash in the usual manner. The salt obtained, after purification, was dried between filter-paper and analysed.

0·2464 gram lost 0·0247 gram at 100—120° and gave 0 1157 gram K_2SO_4.

	Theory. $C_6ClBrK_2O_4,2OH_2$	Found.
H_2O	9·84 per cent.	9·97 per cent.
K	21·34 „	21·02 „

The salt was therefore potassium chlorobromanilate, which, as before stated, has been previously obtained by Krause (*loc. cit.*) from metadichlorometadibromoquinone.

It is noteworthy that the decomposition of metadichlorometadibromoquinone by potash is effected with much greater ease than that of chlorotribromoquinone.

The production of metadichlorometadibromoquinone from dichloroparanitrophenol and bromine is represented by the following equation:—

$$C_6H_2Cl_2(NO_2)\cdot OH + 4Br_2 + 2OH_2 = C_6Cl_2Br_2O_2 + 6HBr + HNO_3.$$

III. *Action of Bromine on Parachlororthonitrophenol.*

Parachlororthonitrophenol was prepared both by chlorinating orthonitrophenol and by nitrating parachlorophenol. It was purified by means of its sodium salt, which crystallises from water in red prisms of the formula $C_6H_3ClNO_3Na,H_2O$. On treating this with dilute hydrochloric acid, and crystallising the resulting compound from alcohol, parachlororthonitrophenol was obtained in large, yellow prisms melting at 87°. The recorded melting point is 86—87°.

A known weight of parachlororthonitrophenol was dissolved in glacial acetic acid and treated with one molecular proportion of bromine, the solution being kept cool. After separating the product in the usual manner, it was dissolved in boiling alcohol, from which it was deposited on cooling in large, sulphur-yellow scales melting sharply at 125°. A portion converted into the potassium salt, decomposed with dilute acid and crystallised from alcohol, was found to melt at the same temperature.

If the above compound were a normal bromination product of parachlororthonitrophenol, it would be parachlororthobromorthonitrophenol, and would give bromanil on treatment with bromine and water at 100°, the parachlorine-atom being displaced by one of the oxygen-atoms in the quinone, just as it is in the case of orthoparadichlororthonitrophenol (*vide ante*).

2 grams of supposed parachlororthobromorthonitrophenol was therefore heated with four molecular proportions of bromine and water in the usual way. It was entirely converted into a compound insoluble in alcohol and in potassium carbonate solution, containing bromine but no chlorine. In the solution filtered from the crude substance, however, hydrogen chloride as well as hydrogen bromide was detected. It was crystallised from benzene, dried at 100°, and analysed.

0·2839 gram gave 0·5029 gram AgBr.

	Theory. $C_6Br_4O_2$.	Found
Br	75·47 per cent.	75·52 per cent.

The production of bromanil from this nitro-halogen-derivative affords conclusive evidence that it is parachlororthobromorthonitrophenol.

Potassium Parachlororthobromorthonitrophenol.— This compound crystallises in beautiful, dark-red, anhydrous needles, sparingly soluble in cold water. Analysis:—

0·1807 gram dried at 100° gave 0·0540 gram K_2SO_4.

	Theory. $C_6H_2ClBrNO_3K$.	Found.
K...........	13·42 per cent.	13·39 per cent.

Barium Parachlororthobromorthonitrophenol.—This is not at all a characteristic compound. It is obtained as an orange-yellow precipitate when barium chloride is added to a solution of the potassium salt, also by boiling the phenol with water and barium carbonate. It is only slightly soluble in boiling water, and nearly insoluble in the cold. It is deposited from its solution in boiling water in tufts of orange-yellow needles, resembling in appearance the barium salt of dichlororthonitrophenol, which has the composition $C_6H_2Cl_2NO_3K,2H_2O$. Unlike the crystals of the last-mentioned compound, these needles appear to lose their form on separating them from the mother-liquor. They, however, then contain 1 mol. H_2O. Analysis gave the following numbers:—

I. 0·1427 gram lost 0·0040 gram at 100—120° and gave 0·0503 gram $BaSO_4$.

II. 0·1647 gram gave 0·0591 gram $BaSO_4$.

	Theory. $(C_6H_2ClBrNO_3)_2Ba,H_2O$	Found I.	Found II	
H_2O	2·70 per cent.	2·80	—	per cent.
Ba.........	20·82 „	20·74	21·06	„

The anhydrous salt is much darker in colour than the hydrated.

Calcium Parachlororthobromorthonitrophenol.—This forms orange-red, glistening scales, very slightly soluble in cold water. Dried between filter-paper, they gave the following result on analysis :—

0·2140 gram lost 0·0177 gram at 100—120° and gave 0·0531 $CaSO_4$.

	Theory. $(C_6H_2ClBrNO_3)_2Ca,2\frac{1}{2}H_2O$	Found.
H_2O..........	8·21 per cent.	8·31 per cent
Ca	7·17 „	7·28 „

At this stage of my experiments, I learnt from Dr. Armstrong that a chlorobromonitrophenol had lately been obtained in his laboratory by the action of bromine and water at 100° on parachlorodiorthonitrophenol, m. p. 80·5°. From the manner in which it was produced, this compound ought to be identical with the one just described, but from the appearance of the potassium-derivative, which was in red scales, such did not seem to be the case. It seemed probable, therefore, that at the moment of substituting bromine for nitroxyl, isomeric change had taken place. The following experiments were made in order to investigate this matter.

10 grams of parachlororthonitrophenol, m. p. 87°, was dissolved in acetic acid and the solution boiled with one molecular proportion of bromine for half an hour in a flask attached to a reflux condenser. It was then left to cool for some hours, separated in the usual way, and crystallised from alcohol, from which it separated in yellow prisms melting at 120°. A portion was converted into the potassium salt, which was obtained in red anhydrous plates, agreeing with Dr. Armstrong's description. A specimen of this salt dried at 100° was then analysed :—

0·1639 gram gave 0·0500 gram K_2SO_4.

	Theory. $C_6H_2ClBrNO_3K$.	Found.
K	13·42 per cent.	13·66 per cent.

It is thus seen that the compound obtained by brominating parachlororthonitrophenol at a temperature near to 100° is isomeric and not identical with that obtained by performing the same experiment at the ordinary temperature, and this being the case it became of interest to try whether any change took place when parachlororthobromorthonitrophenol, m. p. 125°, was heated with a small quantity of bromine; for this purpose—

I. 5 grams of parachlororthobromorthonitrophenol was dissolved in the minimum quantity of glacial acetic acid and heated at 100° in a bottle with one-tenth of a molecular proportion of bromine. From the crystalline form of the potassium salt, and also from the appearance and melting point of the phenol itself, it was concluded that the compound was not altered by this treatment.

II. 5 grams of parachlororthobromorthonitrophenol was dissolved in glacial acetic acid and heated for several hours at 100° with one-fifth molecular proportion of bromine.

The product on conversion into the potassium salt was obtained in red laminæ identical in appearance with that obtained by brominating parachlororthonitrophenol at the higher temperature, and the compound obtained on treating the salt with acid and crystallising from alcohol melted at 119°.

III. 5 grams of parachlororthobromorthonitrophenol was dissolved in glacial acetic acid and heated as in the last experiment with half a molecular proportion of bromine. A considerable amount of decomposition had taken place in this instance, and some of the product was insoluble in potassium carbonate solution. The potassium salt was, however, obtained in plates, and the phenol from this melted at 119°.

This compound was, in all probability, orthochloroparabromorthonitrophenol, and in order to verify this a portion was heated with bromine and water, and the resulting quinone-derivative analysed as follows:—

5 grams of the substance was heated with four molecular proportions of bromine and water in the usual manner. The product obtained was crystallised from acetic acid. It contained both chlorine and bromine. A specimen dried at 100° was analysed.

0·2349 gram gave 0·4350 gram $AgCl(AgBr)_3$.

	Theory. $C_6ClBr_3O_2$.	Found.
Cl.......... Br..........	} 72·59 per cent.	72·21 per cent.

The production of chlorotribromoquinone from this compound, and of bromanil from parachlororthobromorthonitrophenol, leaves no doubt that it was orthochloroparabromorthonitrophenol.

Potassium Orthochloroparabromorthonitrophenol.—This salt has been already described in a previous portion of the paper. It may be added, however, that in addition to its differing in crystalline form from potassium parachlororthobromorthonitrophenol it is much lighter in colour than the latter.

Barium Orthochloroparabromorthonitrophenol.—This is obtained as an orange-yellow precipitate when barium chloride is added to a solution of the potassium salt in water; it is very similar in appearance to the corresponding derivative of the isomeric compound.

Calcium Orthochloroparabromorthonitrophenol.—This salt forms red crystals, much darker in colour than the isomer and differing in the amount of water of crystallisation it contains. It loses 3 mols. H_2O at 100—120°, but does not lose the whole until heated for a considerable time at 250°.

I. 0·3245 gram lost 0·0601 gram at 100—250° and gave 0·0681 gram $CaSO_4$.

II. 0·2301 gram gave 0·0471 $CaSO_4$.

	Theory. $(C_6H_2ClBrNO_3)_2Ca,7OH_2$.	Found. I.	 II.	
H_2O	18·83 per cent.	18·52	—	per cent.
Ca........	5·97 „	6·16	5·99	„

Orthochloroparabromorthonitrophenol was prepared, for the sake of comparison with that obtained by isomeric transformation, from parabromorthonitrophenol, m. p. 88°, by chlorinating it in acetic acid solution.

The potassium and calcium salts agree in all respects with those previously described. The following results have been obtained on analysis:—

Potassium Salt.

0·2072 gram dried at 100° gave 0·0605 gram K_2SO_4.

	Theory. $C_6H_2ClBrNO_3K$.	Found.
K..........	13·43 per cent.	13·08 per cent.

Calcium Salt.

0·2346 gram lost 0·0438 gram at 100—250°, and gave 0·0479 $CaSO_4$.

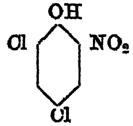
	Theory. $(C_6H_2ClBrNO_3)_2Ca,7H_2O$.	Found.
H_2O........	18·83 per cent.	18·62 per cent.
Ca	5·97 „	5·96 „

The melting point of pure orthochloroparabromorthonitrophenol is 117°. It has been found, however, that if it be mixed with the slightest trace of the isomeride, the melting point is considerably raised. This will perhaps account for the slightly higher melting point of the compound when it is obtained from its isomeride.

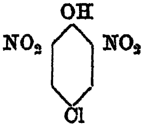
Although the foregoing results are, as regards theoretical considerations, somewhat involved, there are a few points in connection with them which demand attention.

It is seen that by the action of bromine and water at 100° on dichlororthonitrophenol, that portion of the substance which is not converted into a quinone-derivative remains unaltered, and it thus differs from dibromorthonitrophenol, which, when similarly treated, yields, as I have already shown (this vol., p. 147), among other compounds orthobromoparaorthodinitrophenol (m. p. 116°), the second nitro-group being introduced by means of the nitric acid produced from the nitroxyl liberated in the formation of bromanil. It might, therefore, have been expected that a chlorodinitrophenol would have been obtained from dichlororthonitrophenol. According to Petersen (*Annalen*, 157, 164, and *Ber.*, 6, 370), when dichlororthonitrophenol is warmed with concentrated nitric acid, it yields parachlorodiorthonitrophenol (m. p. 80·5°), and it may therefore be inferred from this that the nitric acid generated in the reaction between dichlororthonitrophenol and bromine is not sufficiently concentrated to displace the more firmly attached chlorine-atom.

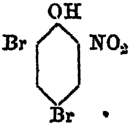
It will, however, at first sight appear anomalous that nitric acid should displace the chlorine-atom occupying the ortho-position in dichlororthonitrophenol, and the bromine-atom occupying the para-position in dibromorthonitrophenol.



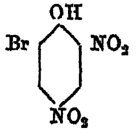
Dichlororthonitrophenol.



Parachlorodiorthonitrophenol.



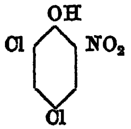
Dibromorthonitrophenol.



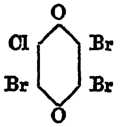
Orthobromoparaorthodinitrophenol.

Dr. Armstrong has shown, however (*Jour. Chem. Soc.*, 1875, 520) that *parabromo*diorthonitrophenol is easily transformed by bromine into the isomeric *orthobromo*paraorthodinitrophenol, and therefore the reaction between nitric acid and dibromorthonitrophenol is probably in the first stage precisely similar to that between nitric acid and dichlororthonitrophenol; that is to say, the bromine-atom in the ortho-position is displaced by NO_2. The parabromodiorthonitrophenol is, however, no sooner formed than it undergoes isomeric change from the presence of free bromine, which, at the temperature employed, would be liberated by even a small quantity of nitric acid in excess.

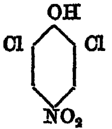
The formation of the quinone-derivatives from these halogen-nitrophenol compounds appears to be in the strictest accordance with what might have been expected, thus:—dichlororthonitrophenol and bromine yield chlorotribromoquinone; dichloroparanitrophenol and bromine yield dichlorodibromoquinone; in like manner parachlororthobromorthonitrophenol yields tetrabromoquinone, and lastly orthochloroparabromorthonitrophenol chlorotribromoquinone.



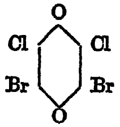
Dichlororthonitrophenol.



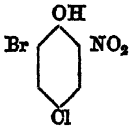
Chlorotribromoquinone.



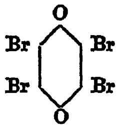
Dichloroparanitrophenol.



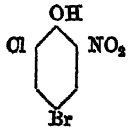
Metadichlorometadibromoquinone.



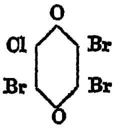
Parachlororthobromorthonitrophenol.



Tetrabromoquinone.



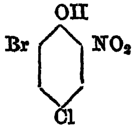
Orthochloroparabromorthonitrophenol.



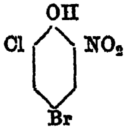
Chlorotribromoquinone.

It will, I think, be admitted that the above concurrence with theoretical views sufficiently justifies my adopting these decompositions as a means of establishing the constitution of the two isomeric chlorobromonitrophenols.

With reference to the isomeric change of parachlororthobromorthonitrophenol to orthochloroparabromorthonitrophenol, whatever may be the nature of the reaction, it appears to take place more easily when parachlororthonitrophenol is treated with bromine at 100° (and possibly also in Dr. Armstrong's experiment, to which I have already referred, when parachlorodiorthonitrophenol is similarly treated), than when parachlororthobromorthonitrophenol is heated with a small quantity of bromine.



Parachlororthobromorthonitrophenol. M. p. 125°.



Orthochloroparabromorthonitrophenol. M. p. 117°.

This may be because it occurs simultaneously with the exchange of hydrogen for bromine. It is well known that ortho- and paranitrophenols are incapable of exchanging more than two atoms of hydrogen for halogen,* and it would therefore be expected that a dihalogen-derivative such as parachlororthobromorthonitrophenol would be more or less indifferent towards reagents. Since no other compound is formed, there can be no doubt whatever that the change is intramolecular.

I hope to still further continue my experiments in this direction.

In conclusion, I must again express my thanks to Professor Armstrong for his much-valued advice.

LXXX.—*The Effects of Dilution and the Presence of Sodium Salts and Carbonic Acid on the Titration of Hydroxylamine by Iodine.*

By TAMEMASA HAGA.

ALTHOUGH hydroxylamine in solution is readily oxidised by many reagents, its estimation volumetrically is more or less interfered with by the fact that the products of its oxidation may vary. Meyeringh and others have shown that cupric hydroxide, permanganic acid, and other oxidising agents give irregular results. Titration with free iodine in non-acid solutions is the only method which has yet been proved to be fairly trustworthy. With this method, I have become very familiar in connection with researches carried out, not only by myself, but by my former colleagues, Mr. Kawakita and Mr. Shimidzu, in conjunction with Dr. Divers, under whom we had studied, and I have long been aware that it is accurate only when the conditions are comparatively uniform. In order to learn what variations in the process, as ordinarily carried out, might cause the irregularities I at times observed in the results, I made, last winter, a series of estimations of a known quantity of hydroxyammonium chloride, under definitely varied conditions, the results of which furnish the matter for this communication.

---

* Numerous attempts have been made to prepare tri- and tetra-halogen-derivatives of ortho- and para-nitrophenols; and as late as last year Kollrepp (*Annalen*, **234**, 1) made an unsuccessful experiment to prepare trichloroparanitrophenol by the action of potassium chlorate and hydrochloric acid on paranitrophenol.

The volumetric estimation of hydroxylamine is performed by adding a decinormal solution of iodine in potassium iodide to the hydroxylamine solution in presence of alkali bicarbonate, so long as it is bleached, generally using starch as an indicator. In order to get the best results, I find, firstly, that the solution for titration should not be excessively dilute, and, secondly, that it should contain very little alkali salts, and, accordingly, neither contain, to begin with, much acid—for this needs to be neutralised—nor receive during titration more sodium bicarbonate than is necessary to take up the hydrogen iodide formed. The hydroxyammonium chloride used in all my experiments was prepared from mercury fulminate.

Influence of the Strength of the Solution.—Very concentrated solutions of hydroxyammonium chloride give results which are too low. For example, 5 c.c. of a solution of which the true titer was 10 c.c. of decinormal iodine solution, required, after evaporation to dryness, and addition of a few drops of sodium bicarbonate solution, 9·3 c.c. only of iodine; 5 c.c. of another solution with a titer of 9·9 c.c. iodine solution, required, after evaporation, only 9·4 c.c.; and 5 c.c. of a third solution with a titer of 9·55 c.c. iodine, required, after evaporation, only 9·25 c.c., the difference not being due to loss during evaporation, but to irregular reaction with the iodine. Moderately concentrated solutions give good results, but when the dilution reaches about 1000 to 1 the results become too high, and more and more so with increase of the dilution. With a dilution of 3000 to 1, the results of the titration are markedly too high, as may be seen from the first of the tables which follow.

With an iodine solution approximately decinormal, and containing 0·1256 gram in 10 c.c., a solution of hydroxyammonium chloride was used containing 0·0330 gram in 10 c.c., and requiring by calculation 9·6 c.c. of the iodine solution. Of this, 10 c.c. were taken for each experiment.

Dilution.	c.c. of iodine solution required.			
	(1.)	(2.)	(3.)	(4.)
Undiluted.............	9·55	9·65	9·55	9·55
Diluted to 100 c.c.	10·1	10·3	10·0	10·0
„ 200 „	10·15	10·25	10·2	10·2
„ 500 „	10·9	10·95	10·7	10·7

A single drop of the iodine solution, added to 500 c.c. of water containing a little sodium bicarbonate, gave in the absence of hydroxylamine a strong colour-reaction with starch; so that dilution of the reagent was not the cause of the greater quantity of it required by the attenuated hydroxyammonium chloride solutions.

But by largely diluting the hydroxyammonium chloride some dissociation of the salt appears to take place, for the iodine solution is consumed to some extent by the diluted solutions, while it is not at all attacked by the stronger ones in the absence of sodium bicarbonate. The following results show this. The solutions used were the same as before, but no addition of sodium bicarbonate was made.

Dilution.	c.c. of iodine solution required.
Undiluted	0·0
Diluted to 100 c.c........	0·4
„ 200 „	0·8
„ 500 „	1·4

Probably dependent on this dissociation is the partial decomposition, on standing for some hours, of hydroxylamine in very dilute solutions of its hydrochloride. Dilution of 10 c.c. of the hydroxyammonium chloride solution to 500 c.c., and of another 10 c.c. to 1000 c.c. was made, and the solutions left all night and then titrated by iodine, with the usual addition of sodium bicarbonate. The 500 c.c. required then only 10·1 c.c. of iodine solution instead of about the 10·8 c.c. which would have been wanted with that dilution if the titration had been proceeded with at once, as may be seen from the first of the preceding tabular statements. The effect of time on the dilution to 1000 c.c. was still more marked, for this required only 8·8 c.c.

Influence of Sodium Chloride, Sulphate, or Carbonate present in the Solutions.—Large excess of sodium bicarbonate gives high results, but I have not made any systematic series of measurements of its effects, for the use of unnecessary quantities can always be avoided. In many cases which occur during investigations, however, the solution of hydroxylamine to be titrated is very acid, and to neutralise this acid with the bicarbonate is to charge the solution with sodium chloride or sulphate, and carbonic acid. Now either of these salts, when present in rather large proportions, affects the titration of the hydroxylamine, while the carbonic acid is also active in this way in presence of one of these salts, although by itself it appears to be without action. Free acid should therefore be nearly all removed—hydrochloric acid by evaporation, sulphuric acid by addition of baryta—before the sodium bicarbonate is added. The effect of sodium chloride was measured in a series of experiments which are tabulated below. The solutions employed were—

Hydroxyammonium chloride	6·9772	gram per litre.
Iodine	12 6238	„
Sodium chloride................	100·0	„

The same, charged with carbonic acid.

5 c.c. of hydroxyammonium chloride, equivalent to 10·1 c.c. of iodine solution, were used in each trial, after dilution to the volume shown in the table by addition of either water, salt solution, or salt solution carbonated.

Diluent.	Vols. of the diluted 5 c.c. hydroxyammonium chloride.					
	15	25	35	45	55	65
	c.c. of iodine solution required.					
Water................	10·2	10·25	10·4	10·45	10·55	10 65
Salt solution	—	10·45	10·7	11·0	11·25	10·85
Salt solution carbonated.	10 4	10·8	10·8	10·9	11 5	12·10

Other results, confirming those in the above table, were obtained with different solutions. Blank tests showed that the diluents of themselves consumed no iodine.

The influence of carbonic acid becomes more marked, at least with lower degrees of dilution of the hydroxylamine solution, when, instead of employing sodium chloride solutions, charged with the gas by sending a stream of it through them for an hour, solutions are prepared in imitation of what happens when an acid solution of hydroxylamine is neutralised, previous to titration, by mixing equivalent volumes of hydrochloric acid and sodium carbonate. The strength of the solutions employed to show this were—

Hydroxyammonium chloride	6·8220	grams per litre.
Iodine (as in last series)	12·6238	,,
Sodium carbonate (anhydrous)	96 3075	,,
Hydrochloric acid..................	64·5079	,,

The acid was equivalent strength to the carbonate.

5 c.c. of the hydroxyammonium chloride solution, equivalent to 9·9 c.c. of the iodine solution, were used in each case, and diluted, to the extent stated in the table, by addition, after the water when this was also used, first of the acid and then of the same volume of the carbonate. A little bicarbonate was added as usual during titration.

Acid and carbonate, c.c. of each.	Total vols. of the diluted 5 c.c. of hydroxyammonium chloride.							
	15	25	35	45	55	65	75	85
	c.c. of iodine solution required.							
0	9·95	10·1	10·2	10·3	10·25	10·45	10·5	10 6
5	10·7	10·7	10·6	—	11·2	—	11·2	—
10	—	11 2	—	11·4	—	11·7	—	—
15	—	—	11·0	—	11·2	—	11·7	—
20	—	—	—	11·7	—	12·0	—	—
25	—	—	—	—	11·35	—	12·0	—
30	—	—	—	—	—	12·0	12·3	—

Blank tests showed that the diluents alone decolorised no iodine.

A corresponding series of trials were made with sulphuric acid in place of hydrochloric acid. The solutions used were—

Hydroxyammonium chloride	6·6492	grams per litre.
Iodine (as before)..................	12·6238	,,
Sodium carbonate (as before)........	96·3075	,,
Sulphuric acid	89·0409	,,

5 c.c. of the hydroxyammonium chloride, equivalent to 9·65 c.c. of iodine solution, were used in each case, and diluted on the same plan as before to the extent shown in the table—

Acid and carbonate, c.c. of each.	Total vols. of the diluted 5 c.c. hydroxyammonium chloride.						
	15	25	35	45	55	65	75
	c.c. of iodine solution required.						
0	9·7	10·0	9·95	10·0	10·0	10·0	10·2
5	10·3	10·35	10·55	—	10·45	—	10·6
10	—	10·7	—	10·65	—	10 6	11·0
15	—	—	10·8	—	10·4	—	—
20	—	—	—	11·0	—	10·85	11·3
25	—	—	—	—	11·2	—	—

The experiments here recorded show that high dilution with water causes hydroxylamine to give a higher titer with iodine than that calculated; that this effect of dilution is increased when sodium salts are present in large amount; and that it is still more increased when carbonic acid is also present. They also show that with very high strength of the solution the titer may be too low. It would seem, therefore, that there must be some deviations from the reaction which is expressed by the equation—

$$2NH_3O + 2I_2 = N_2O + 4HI + H_2O.$$

Should the action of iodine not go so far, nitrite would be formed, and the low results obtained with very concentrated solutions be accounted for. The production of nitrite from hydroxylamine by various oxidising agents has been noticed by Bertoni, so that its formation through the action of iodine would not be improbable. On examination, I have found that a distinct formation of nitrite does take place, and that, too, not only where concentrated solutions of hydroxylamine are acted upon, but in all cases, even in those where the iodine titer is higher than that indicated by the above equation.* This fact renders still more probable the assumption that the hydroxylamine in decomposing must yield a very little deoxidised nitrogen, either in the free state or in union with iodine. Evidence of the correctness of this view seems to be afforded by a remarkable phenomenon to be observed in titrating hydroxylamine with iodine. A very weak solution being mixed with very little sodium bicarbonate, insufficient for the complete titration by iodine, the solution of the latter is added just beyond the point when it is no longer bleached. If now to this solution a little more sodium bicarbonate is added, a milkiness soon appears, strikingly resembling that of iodoform appearing under similar conditions when in place of hydroxylamine a trace of alcohol is present. It disappears on adding more iodine, but may be reproduced several times in succession before the hydroxylamine is exhausted. The substance causing this turbidity may perhaps be in reality an iodamine related to nitrogen as iodoform is related to carbon.

---

* The solution after titration always yields a little free iodine when acidified, and this, in absence of any iodate in the potassium iodide used, is one proof of the presence of nitrite. The solution also, when freed first from all iodide, and then tested with acidified ferrous sulphate, always gives the brown colour caused by a nitrite.

I am much indebted to Dr. Divers for suggestions in carrying out this investigation.

LXXXI.—*The Action of Light on the Hydrides of the Halogens in Presence of Oxygen.*

By Arthur Richardson, Ph.D., Lecturer on Chemistry, University College, Bristol.

It has been observed by Leo Backelandt (*Bull. Acad. Belg.* [3], **11**, 194), and by McLeod (Trans., 1886, **49**, 686) that hydrochloric acid is partially decomposed when exposed to the combined action of atmospheric oxygen and sunlight, chlorine being at the same time liberated; in order to ascertain the conditions which regulate this change I have been led to make some experiments on gaseous hydrogen chloride, extending the enquiry to the behaviour of hydrogen bromide and iodide, under the following conditions:—

(1.) When the moist gases are exposed to sunlight,

- (*a.*) In presence of enough oxygen to oxidise the whole of the hydrogen to water.
- (*b.*) In presence of a large excess of oxygen.

(2.) When the dry gases are exposed to sunlight under similar conditions.

Bulbs of about 300 c.c. capacity were filled with a mixture of the gaseous hydride and oxygen, obtained in the required proportions by first filling the bulbs with oxygen, pumping out a portion equivalent to the volume of the hydride required, and allowing the latter to flow into the partially exhausted bulb until the pressure was equal to that of the atmosphere; the bulbs were then sealed before the blowpipe.

1. *Hydrogen Chloride.*

This gas was prepared from pure sulphuric acid and sodium chloride; the oxygen employed was purified from any chlorine it might contain by passing it through a strong solution of sodium hydrate. In order to analyse the contents of the bulbs after exposure to light, they were opened under water whereby any chlorine compounds present were absorbed; this solution was then made up to known volume and divided into two parts; in the first part, all the chlorine was converted into chloride, and the total chlorine determined by standard solution of silver nitrate; whilst in the second portion the chlorine capable of liberating iodine from iodide of potassium was estimated by standard sodium thiosulphate, potassium iodide, and starch. No attempt was made in these experiments to discriminate between free chlorine and hypochlorous acid, but the results were calculated as free chlorine; later experiments, however, have led me to believe that a portion of the chlorine was present as hypochlorous acid or some other oxy-acid of chlorine.

1st *Experiment.*—Moist gaseous hydrogen chloride and moist oxygen were mixed together in the proportion of 4 vols. of hydrogen chloride to 1 vol. oxygen, the proportions necessary for the complete oxidation of the hydrogen; the bulb containing this mixture was exposed to sunlight for 24 days, from June 29th till July 23rd; an analysis of the contents of the bulb gave—

Total chlorine	0·16170	gram.
Free chlorine	0·00056	„
Percentage of free chlorine	0·34000	„

The bulb was found to contain free oxygen at the end of the experiment.

2nd *Experiment.*—A bulb was filled with moist hydrogen chloride and oxygen mixed in the proportion of 4 vols. of the chloride to 8 vols. oxygen, giving a large excess of oxygen over that required for complete oxidation. This mixture was exposed to sunlight for 21 days (from June 20th to July 11th). After five days, the gas in the bulb was distinctly greenish. On analysis it gave—

Total chlorine	0·112	gram.
Free chlorine	0 083	„
Percentage of free chlorine	73·810	„

It will be seen that the difference in the results obtained in the two cases is very marked, and it would appear that when hydrogen chloride is mixed with a large excess of oxygen the reaction goes almost entirely in one direction, water and chlorine being formed, and that under these conditions there is little opportunity for the chlorine and water to react to form hydrogen chloride and oxygen. I hope to further investigate this part of the subject, and to determine more fully how far chlorine is capable of decomposing water in the presence of varying proportions of oxygen.

3rd *and* 4th *Experiments.*—Two bulbs were prepared as in the last experiment and exposed to sunshine for 57 days (June 27th to August 25th); at the end of this time the gas in the bulbs contained considerable quantities of free chlorine. I did not, however, succeed in estimating the percentage amount of free chlorine present in these bulbs, although the result obtained was interesting as pointing to the possible presence of hypochlorous acid (or other oxy-acid of chlorine), together with the free chlorine. In these two experiments, the bulbs were opened under weak solution of sodium hydrate, in order to ensure complete absorption of chlorine; the free chlorine was then estimated in the acidified solution as before.* Now if all the liberated chlorine were present in the bulbs as free chlorine, one half of it would be converted into hypochlorite of sodium on absorption with sodium hydrate, and consequently the number obtained by titration with sodium thiosulphate would require to be doubled; on the other hand this would make the total free chlorine too high if part of the chlorine was already present as hypochlorous acid before absorption with sodium hydrate. In both these bulbs the numbers representing the free chlorine calculated as such exceeds the amount of total chlorine as determined by standard solution of silver nitrate; analyses gave—

	I.	II.
Total chlorine........	0·188 gram.	0·177 gram.
Free chlorine	0·247 „	0·299 „

From these analyses, it may be supposed that some of the chlorine was originally present as hypochlorous acid; the relative amounts of free chlorine and hypochlorous acid formed in this reaction will be a subject for further experiments.

5th Experiment.—The action of dry oxygen on dry hydrogen chloride in sunlight was next investigated; the gases were dried over phosphorus pentoxide, and two bulbs were filled with the gases mixed as in the last experiment (4 vols. hydrogen chloride to 8 vols. oxygen). The first bulb was exposed for 27 days (June 20th—to July 17); the gases were then absorbed in water and tested with potassium iodide and starch; no trace of free chlorine could be detected in the solution. The second bulb was exposed for a much longer period, 63 days (June 20th—August 22nd); on analysis of the contents, it was found to contain—

Total chlorine..............	0·341 gram.
Free chlorine absent.	

Hence it would appear that dry hydrogen chloride is perfectly stable in presence of dry oxygen in sunlight. Three bulbs were next filled with hydrogen chloride and oxygen mixed in the same proportions as before, the hydrogen chloride was however saturated with moisture whilst the oxygen was thoroughly dried; this gave a gaseous mixture, which was only partially saturated with water vapour. The bulbs were exposed for 60 days, and their contents then tested for free chlorine; in no case was a trace of this substance detected; here it will be observed that the mixture of hydrogen chloride and oxygen is perfectly stable, even in the presence of aqueous vapour, provided liquid water is absent.*

---

* In estimating the total chlorine, the oxy-acids of chlorine possibly present were decomposed by solution of sulphur dioxide, the excess of which was removed before titration with standard solution of silver nitrate.

2. *Hydrogen Bromide.*

The gas was best prepared by allowing bromine to come in contact with moist amorphous phosphorus, and passing the gas evolved through a tube containing amorphous phosphorus to remove any bromine.

Considering how prone a solution of hydrogen bromide is to decompose with liberation of bromine, it might be supposed that the gas would react similarly under the combined influence of oxygen and sunlight.

1st Experiment.—A bulb was filled with a mixture of moist hydrogen bromide and moist oxygen in the proportions of 4 vols. of hydrogen bromide to 1 vol. oxygen; after exposing this mixture to sunlight for forty-six days (July 5—August 20), the gases were analysed:—

Total bromine................	0·500 gram.
Free bromine........	0·032 „
Percentage of free bromine	0·640 „

2nd Experiment.—Next the mixture of moist hydrogen bromide and oxygen was so prepared as to give a large excess of oxygen (1 vol. of the bromide and 1 vol. oxygen), and a bulb containing this mixture was exposed for 46 days as before; analysis gave the following results:—

Total bromine................	0·323 gram.
Free bromine	0·025 „
Percentage of free bromine	7·730 „

Here again the influence of mass is to be noticed in the case of the oxygen present, for although there was excess of oxygen in both experiments, the large excess in the last instance promoted the decomposition of the acid.

3rd Experiment.—Hydrogen bromide and oxygen, dried over phosphoric anhydride, were mixed in the proportion of 1 vol. of the bromide to 2 vols. of oxygen, and exposed in a bulb to sunlight for 40 days—July 11—August 20; when the contents of the bulb were tested with potassium iodide and starch, no trace of free bromine could be detected, and hence it would appear that dry hydrogen bromide in presence of oxygen is not decomposed by the solar rays.

---

* The gases in Experiments 2, 3, and 4, deposited some of their moisture on the slightest change of temperature, thus providing the liquid water required to start the reaction.

3. *Hydrogen Iodide.*

A mixture of moist amorphous phosphorus and iodine was heated, care being taken to keep the iodine in excess; the gas so evolved contained a considerable quantity of iodine, and an attempt was first made to remove this substance by passing the gas through mercury, the result being, however, that the gas was completely decomposed with formation of mercurous and mercuric iodide and liberation of hydrogen. The gas was finally obtained in a state of purity by passing it through two tubes containing phosphorus pentoxide, whereby all the free iodine was retained in the first tube, imparting a dark-brown colour to the pentoxide, whilst that in the second tube remained white. As might be supposed, gaseous hydrogen iodide shows a strong tendency to decompose under the influence of oxygen and sunlight, though here also the amount of decomposition is to a certain extent dependent on the mass of oxygen present. Two bulbs were filled with a mixture of the moist iodide and oxygen in the proportions of (*a*) 4 vols. of the iodide to 1 vol. of oxygen, (*b*) 4 vols. of the iodide to 8 vols. of oxygen; after an exposure for 20 days, the contents of the bulbs were analysed:—

	a.	*b.*
Total iodine............	0·721 gram.	0·2850 gram.
Free iodine	0·684 ,,	0·2738 ,,
Percentage of free sodium	94·310 ,,	96·0800 ,,

Thus the decomposition was found to be greatest in the bulb containing a large excess of oxygen—94·31 per cent. against 96·08 per cent. Free oxygen was found to be present in both bulbs when opened and tested.

Lastly, dry hydrogen iodide was found to be decomposed by dry oxygen, when they were exposed to light in bulbs containing phosphorus pentoxide.

From these experiments, it would appear that in sunlight—

(1.) The stability of the moist hydrides of chlorine, bromine, and iodine is dependent on the mass of oxygen present in excess of that required for their complete decomposition.

(2.) Dry or partially dry hydrogen chloride and bromide are completely stable, even when mixed with a large excess of oxygen.

(3.) Dry hydrogen iodide is decomposed in presence of oxygen.

Note on the Action of Light on Hydrogen Bromide and Iodide, in presence of moist Red Phosphorus.

Some hydrogen bromide was prepared in the manner above described, and then absorbed in water; when the apparatus was exposed to bright sunshine phosphuretted hydrogen was observed to pass over with the hydrogen bromide, and ignited spontaneously on coming in contact with the air. When hydrogen bromide was prepared in the dark, however, no phosphuretted hydrogen was evolved. To discover what occurs in this reaction, an experiment was made in which a bulb containing hydrogen bromide (free from phosphuretted hydrogen) was sealed up together with moist amorphous phosphorus, and exposed to sunlight; after 24 hours cubical crystals made their appearance on the sides of the bulb, and grew to a considerable size in the course of a few days; they had all the appearance of phosphonium bromide, and were decomposed by water with liberation of phosphuretted hydrogen; the reaction may be expressed by the equation—

$$P + 3H_2O + HBr = PH_4Br + H_3PO_3.$$

Hydrogen iodide, when similarly treated, yielded crystals resembling phosphonium iodide. On exposing saturated solutions of hydrogen bromide and iodide, together with amorphous phosphorus, to sunlight, large quantities of phosphonium bromide and iodide were obtained.

LXXXII.—*Note on the Influence of Liquid Water in promoting the Interaction of Hydrogen Chloride and Oxygen on Exposure to Light.*

By Henry E. Armstrong, F.R.S.

The experiments described by Dr. Richardson appear to establish the fact that hydrogen chloride is not oxidised by ordinary oxygen on exposure to sunlight unless water be present; and thus one more is added to the now numerous instances showing that interactions which are commonly assumed to occur between *two* substances more frequently than not are possible only in presence of a third substance —of a *catalyst* as I have elsewhere termed it.

Dr. Richardson states that no chlorine is liberated if only one of the gases be saturated, and that it is necessary to saturate *both* gases with water; on hearing of his results at the recent British Association meeting, I was much struck and also puzzled by this statement. The explanation which he has now given in the foregoing paper that *liquid* water must be present, however, appears to me to be satisfactory, and it is on this point that I venture to offer the following remarks in the hope that I am thereby contributing to the appreciation of the importance of observations of the character of those which he has recorded.

The interaction in question is a parallel case to that of the oxidation of sulphur dioxide so carefully worked out by Professor H. B. Dixon, and which I have already discussed in my paper on "Electrolytic Conduction, &c." (*Proc. Roy. Soc.*, 1886, 288). In gaseous mixtures chemical change appears to take place only when a comparatively high electromotive force—or its equivalent—is employed, one sufficient to produce disruptive discharge being usually required: regarding the interaction as a case of electrolysis, a gaseous mixture of HCl, O_2 and OH_2 might therefore be expected to prove insensitive to light. But an aqueous solution of hydrogen chloride is one of the best of liquid conductors, and it is easy therefore to understand that a relatively small electromotive force should suffice to electrolyse a *liquid* system of the same three elements.

From this it should follow that a moist mixture of HCl and O_2 which is affected at ordinary temperatures would prove to be insensitive to light if the temperature be raised sufficiently to gasify the water. It is also probable that a *gaseous* mixture of chlorine and water will be found insensitive to light, provided that the temperature be high enough to destroy all *molecular aggregates* of the two substances: this proviso appears to me to be necessary as I imagine it is possible that in a molecule which includes both chlorine and water the direct absorption of light energy may induce a rearrangement ending in the formation of hydrogen chloride and oxygen.

The study of the effect of light on mixtures of H_2, Cl_2 and water at temperatures high enough to gasify the water would be of interest from this point of view; probably it will be very difficult to entirely hinder the formation of surface layers of liquid and thus prevent any action taking place, but Professor Dixon's observations on the influence of the amount of gaseous water on the rate of propagation of explosive waves encourage us to hope that the required information may be gained in such a case by studying the rate of change at various temperatures.

It may be pointed out that Dr. Richardson's observation on a mixture of dry hydrogen iodide and oxygen is inconclusive owing to his having allowed phosphoric oxide to be present with the gases: this substance appears almost invariably to contain either phosphorus or lower oxides.

LXXXIII.—*On the Magnetic Rotation and Densities of Chloral, Chloral Hydrate, and Hydrated Aldehyde.*

By W. H. Perkin, Ph.D., F.R.S.

In a paper brought before the Society last year (*Chem. Soc. Trans.*, 1886, 777), it was shown that the study of the magnetic rotation of hydrated products was calculated to throw much light upon their nature, and show whether they are true chemical or atomic compounds, or only molecular products containing water, because, if of the first class, the rotation should be less than the sum of the rotations of the compounds and water used in their preparation; but if of the latter, the rotation should be the same as that of the compounds and water. It appeared to me that it would be of interest to apply this method to the examination of chloral hydrate, and thus get a further insight into the nature of this interesting compound, which has been the subject of so much discussion at different times.

Chloral.

Before the examination of chloral hydrate itself could be commenced, it was necessary to determine the magnetic rotation of chloral. The product used was obtained from Kahlbaum. It was purified first by agitation with phosphoric anhydride, then decanted and afterwards distilled from a little fresh anhydride.

It came over between 95° and 98°, but after carefully fractioning a few times, more than half was obtained boiling between 97·8 and 98·1°. corr. (Thorpe found 97·2°.) This was then refractioned into three equal quantities, rejecting a little of the first and last parts, and the densities taken of the first and third fraction. The numbers obtained were—

I. B. p. 97·6°. $d\frac{9°}{9°}$ 1·5293.

III. B. p. 97·9—98·1°. $d\frac{9°}{9°}$ 1·5292.

The product was, therefore, nearly homogeneous. Fraction III was selected for examination; its density determination gave—

$d\frac{9°}{9°}$ 1·5292,

$d\frac{15°}{15°}$ 1·5197,

$d\frac{25°}{25°}$ 1·5060.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·2206	6·597
15·2	1·2166	6·575
15·3	1·2194	6·590
16·5	1·2237	6·608
17·1	1·2192	6 591
19·0	1·2165	6·584
Average 16·3	1·2193	6·591

Chloral Hydrate.

The specimen of this product employed was beautifully crystallised. It was powdered, and after it had been kept under a bell-jar over sulphuric acid for some time it was melted. It distilled at 96·6—97·2°, a little at last coming over at 98 6°.

This substance being solid at the ordinary temperature, its density and magnetic rotation had to be determined when it was in a melted condition. The special arrangements of apparatus used for these purposes I hope to give in a future paper.

The following numbers were obtained for its relative densities; they are averages of two sets of determinations :—

$$d\frac{49{\cdot}9^\circ}{49{\cdot}9^\circ}\ 1{\cdot}6415,$$

$$d\frac{58{\cdot}4^\circ}{58{\cdot}4^\circ}\ 1{\cdot}6274,$$

$$d\frac{66{\cdot}9^\circ}{66{\cdot}9^\circ}\ 1{\cdot}6136,$$

The determination of the magnetic rotation gave—

t.	Sp. rotation.	Mol. rotation.
51·0°	1·2691	7·120
53·2	1·2633	7·105
55·5	1·2621	7·116
59·8	1·2775	7·231
56·0	1·2746	7·186
54·9	1·2729	7·167
54 0	1·2694	7·141
52·8	1·2713	7·141
Average 54·6	1·2700	7·151

The temperature at which these observations were made being rather high, it was thought desirable to make others at lower temperatures: the only way to do this was to employ solutions of chloral hydrate. An aqueous solution was the first examined. It was made as strong as possible, the proportions corresponding to three molecules of water to one molecule of chloral hydrate. This deposits crystals on standing for a few hours, but as these redissolve on the application of heat and the solution then remains clear for several hours, plenty of time is obtained to make the necessary observations. Chloral hydrate dissolves in water with fall of temperature, as is well known.

The relative density determinations gave—

$d\frac{4^\circ}{4^\circ}$ 1·49032, $d\frac{45^\circ}{45^\circ}$ 1·4632,
$d\frac{15^\circ}{15^\circ}$ 1·48033, $d\frac{55^\circ}{55^\circ}$ 1·4590,
$d\frac{25^\circ}{25^\circ}$ 1·47318, $d\frac{65^\circ}{65^\circ}$ 1·4548,
$d\frac{35^\circ}{35^\circ}$ 1·4678, $d\frac{70^\circ}{70^\circ}$ 1·4530.

The magnetic rotations were determined at the ordinary and at a high temperature.

t.	Sp. rotation.	Mol. rotation.
15·2°	1·2196	10·049
15·2	1·2134	9·998
15·6	1·2206	10·058
15·6	1·2140	10 004
15·8	1·2176	10·085
15·8	1·2173	10·083
15·8	1 2104	10·025
10·5	1·2138	9·978
10·5	1 2135	9·971
Average 14·4	1·2162	10·016
56·5°	1·2013	10·043
56·0	1 2008	9·992
56·5	1·1998	10·037
Average 56·3	1·2006	10·024

These numbers give the following values for chloral hydrate:—

	At 14·4°.	At 56·3°.
Chloral hydrate and 3 mols. of water	10·016	10·024
Less 3 mols. water	3·000	3·000
Chloral hydrate	7·016	7·024

As these results are somewhat lower than those obtained from the fused chloral hydrate, experiments were made with a more inactive solvent than water. The solvent selected was isoamyl oxide, as it is difficultly volatile, boiling at 173°, and therefore a solution made with it is not likely to alter in composition, and also because it dissolves chloral hydrate freely.

The densities of isoamyl oxide were taken for a large range of temperature, so that they might be compared with those of the solutions of chloral in the solvent: they gave—

$d\frac{4^\circ}{4^\circ}$ 0·78891, $d\frac{40^\circ}{40^\circ}$ 0·7659,

$d\frac{15^\circ}{15^\circ}$ 0·7806, $d\frac{55^\circ}{55^\circ}$ 0·7585,

$d\frac{25^\circ}{25^\circ}$ 0·7743, $d\frac{70^\circ}{70^\circ}$ 0·7520.

In the first experiment, the solution was accidentally made in the proportion of 1 mol. of chloral hydrate to 0·8797 mol. of isoamyl oxide instead of one molecule of each; this, however, was not very material. Chloral hydrate dissolves in isoamyl oxide with fall of temrature.

The density of the solution was—

$d\frac{4^\circ}{4^\circ}$ 1·1329, $d\frac{45^\circ}{45^\circ}$ 1·0920,

$d\frac{15^\circ}{15^\circ}$ 1·1206, $d\frac{55^\circ}{55^\circ}$ 1·0830,

$d\frac{25^\circ}{25^\circ}$ 1·1113, $d\frac{60^\circ}{60^\circ}$ 1·0789.

$d\frac{35^\circ}{35^\circ}$ 1·1012,

Its magnetic rotation gave four series of numbers exactly the same, so that only one need be given:—

t.	Sp. rotation.	Mol. rotation.
16°	1·1152	16·853

The next series of experiments was made with a solution in the proportion of 2 mols. of chloral hydrate and 1 mol. of isoamyl oxide; this was a supersaturated solution, but when warmed, the crystals dissolved and were not deposited again on cooling for several hours.

The density determination gave the following numbers averaged from two sets of determinations.

$d\frac{15^\circ}{15^\circ}$ 1·2466,	$d\frac{45^\circ}{45^\circ}$ 1·21680,
$d\frac{25^\circ}{25^\circ}$ 1·2366,	$d\frac{55^\circ}{55^\circ}$ 1·2062,
$d\frac{35^\circ}{35^\circ}$ 1·2272,	$d\frac{70^\circ}{70^\circ}$ 1·1890.

The determination of the magnetic rotation gave—

t.	Sp. rotation.	Mol. rotation.
26°	1·1543	25·370
26	1·1498	25·271
26	1·1527	25·330
26	1·1531	25·343
26	1·1525	25·328

These two sets of experiments gave the following numbers for chloral hydrate:—

Rotation of solution 1 mol. of chloral hydrate in 0·8797 isoamyl oxide......................	16·853
Less rotation of 0·8797 mol. isoamyl oxide....	9·825
Chloral hydrate	7·028

Rotation of solution of 2 mols. chloral hydrate in 1 mol. isoamyl oxide ..	25·328
Less 1 mol. isoamyl oxide	11·168
2 mols. chloral hydrate	14·160 ÷ 2 = 7·080

We have therefore the following numbers for chloral hydrate:—

Fused.	In aqueous solution.		In isoamyl oxide solution.	
7·151	7·016	7·024	7·028	7·088

Average omitting the first = 7·037.

It is seen that the fused product has given numbers higher by 0·114 than the average (viz, 7·037) of the four determined from the solutions; this is considerably more than is likely to arise from error of experiment, and is undoubtedly due to a certain amount of dissociation in the chloral hydrate, as will be seen further on, therefore the numbers from the solution are the most trustworthy. In one case, the aqueous solution was examined at a high temperature, and gave numbers nearly the same as those obtained with the same solution at low temperature, but no doubt the excess of water present would prevent dissociation.

If the rotation of chloral be now taken, and subtracted from that of chloral hydrate, it will show whether the water used in the preparation of the latter retains its ordinary value, and therefore exists still as water, or whether it is smaller, and no longer exists as water:—

Chloral hydrate	7·037
Chloral	6·590
Difference	0·447

From this it is evident that chloral hydrate does not contain water as a constituent, otherwise the difference would have been 1·000.

If chloral hydrate then be *trichlorethylidene glycol*, as the foregoing indicates, does its rotation correspond to that of such a compound? To find this, however, we require to know the magnetic rotation of aldehyde and ethylidene glycol, which of course are related to each other as chloral is to trichlorethylidene glycol. The rotation of aldehyde is known, but as ethylidene glycol is too unstable to exist in the pure state at ordinary temperatures. its rotation of course has not been practically determined. Compounds of this glycol, however, are known, and the magnetic rotations of these have been determined, they are acetal and methylacetal, and in my paper published in 1884 (Trans., 1884, 571), the value of ethylidene glycol was deduced as nearly as the data at my disposal permitted. From the rotation of acetal, I obtained 2·974, and from that of methylacetal 2·817 for this substance. Moreover, the rotation of ordinary glycol has likewise been determined, it is 2·943; and it has been shown that ethylidene compounds give lower rotations than do ethylene, therefore the lower number 2·817 was considered the most likely to be correct. This is supported by another consideration. The difference between the rotation of ethylene chloride and ethylidene chloride is as follows:—

Ethylene chloride	5·485
Ethylidene chloride	5·335
Difference	0·150

Now if this difference be subtracted from that of ordinary glycol the result should be very near to that of ethylidene glycol.

Glycol	2·943
Less	0·150
	2·793

This is remarkably close to that deduced from the rotation of methylacetal, so that the mean of these will probably be very near the truth: it is 2·805.

If the value of aldehyde be subtracted from this, we ought to obtain a difference very close to that which should exist between chloral and trichlorethylidene glycol.

Ethylidene glycol (calculated)	2·805
Aldehyde	2·385
Difference	0·420

This is very close to the difference found between chloral and chloral hydrate, therefore the latter substance must be trichlorethylidene glycol. The experiments which have been made upon chloral hydrate by Naumann, Würtz, Moitessier, Engel, and others, and more recently by Ramsay and Young, show that when volatilised its vapour always undergoes dissociation. In the crystalline condition, however, it is a stable product. It was, therefore, of interest to see whether the substance when in the liquid state remained definite in character.

As already remarked, the magnetic rotation of fused chloral hydrate at 54·6° gave high numbers, indicating that dissociation did take place to some extent at this temperature, which is about 42° below its boiling point. To further examine into this matter, it was thought that an examination of the curves obtained by plotting the densities for different temperatures, both of the fused product and its solutions, might throw some additional light on the subject. It was for this reason that so many density determinations at different temperatures were made of the products referred to in the previous part of this paper. The curves relating to chloral and isoamyl oxide are also given for the sake of comparison with those of the less stable products. It is necessary to remember that the densities used are relative to water at the same temperatures, and are not the true densities. The curves are given at the end of this communication.

The densities of chloral at different temperatures* give an ordinary kind of curve, such as is always obtained from relative densities of stable compounds. In the case of chloral hydrate in aqueous solution, a similar result is obtained, showing that chloral hydrate does not dissociate, or at any rate to only a very slight extent, in the presence of water even at temperatures up to 70° (see Plate I). The magnetic rotation at 56° also does not indicate dissociation, or only very little, the minute difference between the rotation at the low and high temperature being within the errors of observation, still they are in the direction required by dissociation, so that it would not be safe to say that no amount of change takes place. Isoamyl oxide gives an ordinary kind of curve, but on examining that given by the densities of a solution of chloral hydrate in isoamyl oxide in the proportion of two molecules of the former to one of the latter, it will be seen that it takes a new direction, and bends to the left instead of to the right; moreover, it is long for the range of temperature. And, lastly, with fused chloral hydrate the part of the curve obtained between 50° and 70° shows that it belongs to one which bends still more to the right, probably taking a direction somewhat similar to that formed by the dotted line; it is also considerably longer for the same range of temperature (see Plate II). That the curve obtained in the case of solution of chloral hydrate in isoamyl oxide should not be so long or so much bent to the right is obvious, because the chloral hydrate is diluted with isoamyl oxide, and this gives a curve in the opposite direction. In the case of the solution in the proportion of 1 mol. of chloral hydrate to 0·8797 mol. isoamyl oxide, which, of course, is a more dilute solution than the above, the influence of the isoamyl oxide prevents the curve from changing to the left hand until a temperature of between 50° and 60° is reached; it is, therefore, not given.

---

* The higher relative densities of this compound were calculated from the expansion given by T. E. Thorpe (Trans., 1880, 192).

It is difficult to determine the exact temperature at which chloral hydrate when in solution in isoamyl oxide commences to dissociate; it certainly occurs between 30° and 40° and probably is lower, in fact there is a difference in the magnetic rotation of the two solutions in isoamyl oxide which tends to show this; thus, the one examined at 26° gave a number for chloral hydrate 0·052 higher than that examined at 16°; this is not much, but is greater than would be expected from errors of observation.

The dissociation of chloral hydrate when in solution so much below its melting point is an interesting fact, because it goes to show that the physical forces connected with crystalline structure have a considerable influence in some cases on the stability of a substance.

As very little is said about the results of hydrating aldehyde by admixture of water, I was induced to make a few experiments in that direction. Gmelin states that aldehyde mixes in all proportions with water, the mixture being attended with rise of temperature, and a mixture of three parts of water to one of aldehyde boils at 37°. Ramsay and Young (*Phil. Trans*, Part I, 1886, 117) say that aldehyde when mixed with water evolves heat, and undergoes contraction; and this behaviour would point to the formation of the dihydric alcohol, $CH_3CH(OH)_2$.

The aldehyde employed in the following experiments was prepared from paraldehyde; the average of three series of density determinations gave—

$$d\frac{-5^\circ}{+4^\circ}\ 0·81312,$$
$$d\frac{0^\circ}{4^\circ}\ 0·80561,$$
$$d\frac{4^\circ}{4^\circ}\ 0·80058,$$
$$d\frac{8^\circ}{4^\circ}\ 0·79520,$$
$$d\frac{13^\circ}{4^\circ}\ 0·78826,$$

As the temperatures commence below 4°, the true densities are given. These are close to those given in my previous paper (Trans., 1884, 475).

Experiments were first made on a mixture of aldehyde and water in equimolecular proportions ($C_2H_4O : H_2O$). On making this some interesting peculiarities were noticed. If the temperature of the liquids and the atmosphere be low, say not higher than 8° or 9°, at the moment of mixing, the temperature drops, it then commences to rise somewhat quickly, and continues to rise more and more slowly for a long time. An experiment with 22 grams of aldehyde and 9 of water, mixed at the temperature of the air in a large test-tube protected with cotton-wool, fell from 7·46° to 5·9° = 1·56°; the temperature then began to rise.

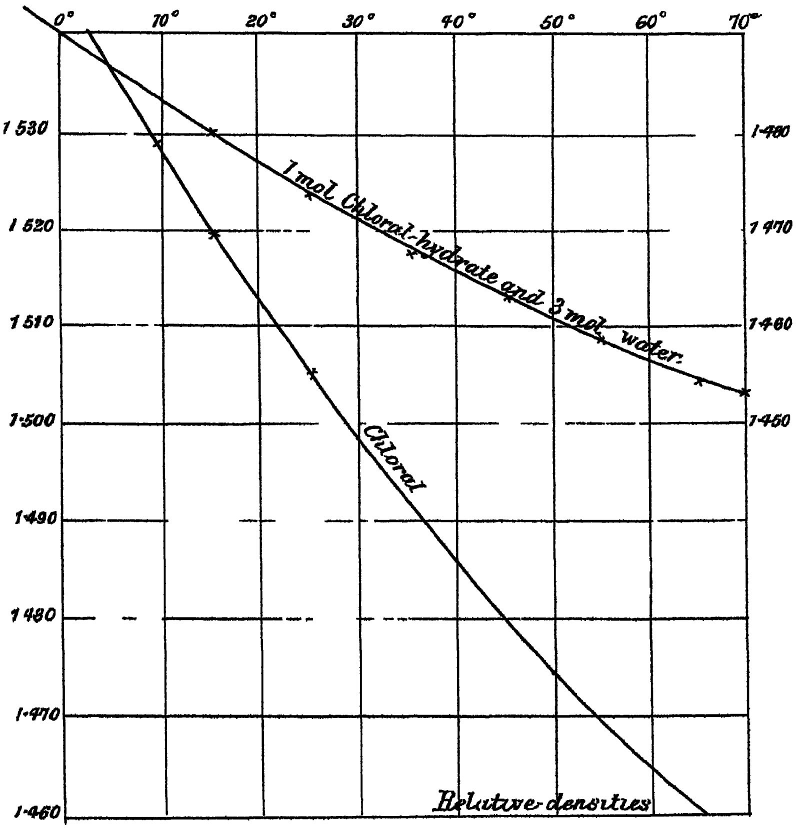
After	1	minute	it was	8·8°
„	2	minutes	„	11·0
„	4	„	„	14·7
„	8	„	„	17·5
„	12	„	„	18·15
„	16	„	„	18·4
„	20	„	„	18·53
„	24	„	„	18·58

It then began to fall very slowly.

If the temperature of the air and products be higher, say 16°, and

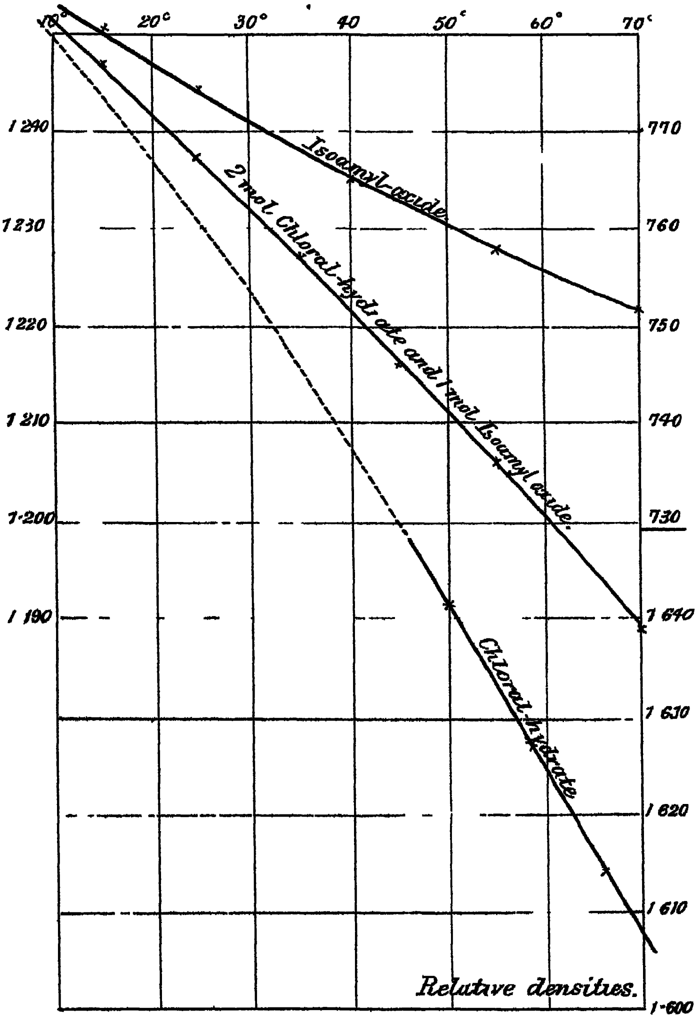
Journ Chem Soc Nov 1887.

PER
11-t



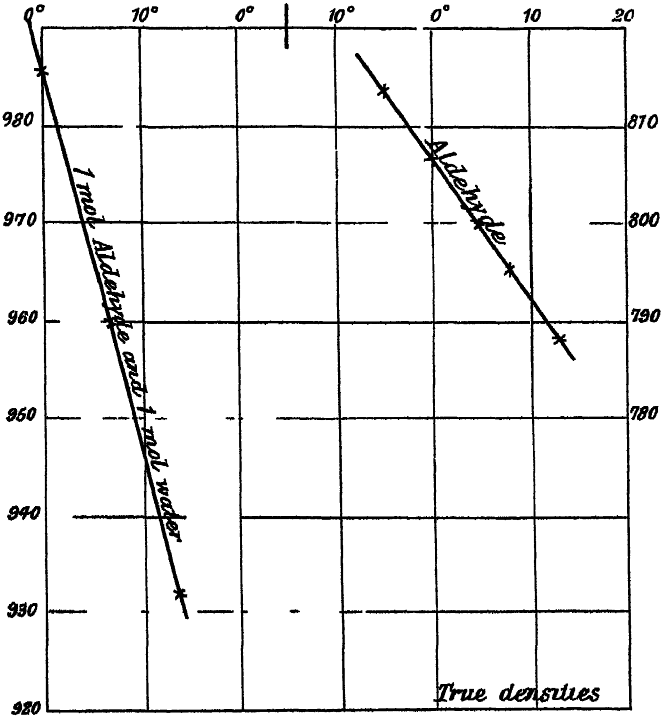
Journ Chem Soc Nov 1887

PERKIN
Plate 2



Journ Chem Soc Nov 1887

PERKIN
Plate 2



the quantities not too small, the rise of temperature is more rapid, and ebullition sets in.

If an additional quantity of water be added to this monohydrated aldehyde, after it is at rest, corresponding to a second molecule ($C_2H_4O : 2H_2O$), it causes an immediate rise of temperature, which reaches its maximum in about four minutes; the rise, however, is about 4° only. If this product is then allowed to stand until cool, the addition of water in the proportion of a third molecule ($C_2H_6O : 3H_2O$), causes the same thing to take place again, but in a still less degree. If this be repeated again, heat is still evolved, but only a little. These experiments were not made with the intention of giving accurate measurements; if done with all precautions, of course, much larger results would be obtained.

The mixture made in equimolecular ($C_2H_4O : H_2O$) proportions was next examined.

On attempting to determine the density of this product, the results at first were most perplexing from the fact that they were not concordant; it was then discovered that this mixture when subjected to a change of temperature does not become constant in volume at the new temperature in less than two hours and a half to three hours or even more, so that it was eventually found necessary to keep the product in the density-tube at the required temperature for this period before adjusting the volume. The following results will illustrate this.

Density determinations at 0°; temperature of product before commencing the experiment, 3°.

After cooling for ¾ of an hour density = 0·9817
" 2½ hours " = 0·98466
" 17 " " = 0·9861

Determinations at 6°; temperature of product before commencing the experiment, 3°.

After warming to 6° for ½ an hour density = 0·9660
" " ¾ of an hour " = 0·9656
" " 2½ hours " = 0·9607
" " 7¾ " " = 0·9606
" " 8½ " " = 0·9603

Determinations at 13°; temperature of product before commencement of the experiment considerably *lower*, but not registered.

After warming to 13° for ¾ of an hour density = 0·9370
" " 2½ hours " = 0·9331
" " 9¼ " " = 0·9330

In the first series, the densities were taken at a *lower* temperature than that of the product used, and it will be noticed that they increase with lapse of time, showing gradual combination. In the second series, the densities were taken at a *higher* temperature than the product used, and here we find a gradual diminution of density with lapse of time due to gradual dissociation.

The densities of this mixture may be taken as—

$$d\frac{0^\circ}{4^\circ}\ 0{\cdot}9861,$$

$$d\frac{6^\circ}{4^\circ}\ 0{\cdot}9603,$$

$$d\frac{13^\circ}{4^\circ}\ 0{\cdot}9330.$$

These numbers show that an extremely large expansion takes place with change of temperature; this will best be seen by comparing the curve they give with that given by the densities of aldehyde (see Plate III). Were this mixture composed of water and aldehyde uncombined, its expansions should be considerably less than that of aldehyde; but there is no doubt that the reduction of volume by cooling is owing to chemical combination chiefly as well as contraction from change of temperature, and, on the other hand, that the expansion is due chiefly to dissociation as well as to expansion from change of temperature. These curves being for the true densities are not strictly comparable with those on the other diagrams.

Monohydrated aldehyde does not solidify when cooled in snow and hydrochloric acid; with the thermometer bulb in the liquid, it boils vigorously at 29—30°.

The magnetic rotations of this product were determined, and gave—

t.	Sp. rotation.	Mol. rotation.
16·2°	0·8922	3·320
16·0	0·8969	3·338
15·8	0·8925	3·320
15·4	0·8940	3·323
15·2	0·8929	3·317
Average 15·7	0·8937	3·324

If the value of aldehyde be subtracted from this, viz., 2·385, we get 0·928 as the difference. As this is less than 1·0 (the value of water), we may conclude that chemical combination had taken place to some extent in the mixture, as shown already by the density determinations. No doubt had the magnetic rotation been determined at a much lower temperature, the difference would have been still smaller, because a larger quantity of the water and aldehyde would have combined to form ethylidene glycol; if all combined, the difference would be about 0·420, as the product would then be the pure glycol. However it was not thought worth the labour to make more determinations as it is very difficult to get the product in a state of equilibrium, and the densities give all the information necessary, though perhaps from the magnetic rotation one might find the percentage of ethylidene glycol formed. It is known that glycols are viscid liquids, and it is interesting to notice that when monohydrated aldehyde is shaken up a froth forms which does not break at once, the mixture differing in this respect both from aldehyde and from water.

Attention has been drawn to the fact that when aldehyde and water are mixed, the first result is the reduction of temperature, the rise of temperature then setting in. This interesting matter is brought out more strongly if absolute alcohol be mixed with aldehyde in equimolecular proportions and the right conditions employed. If the temperature of the air and products be high as in summer time, no effect is noticed except rapid rise of temperature and then energetic ebullition, but if the experiment be made in cold weather, at temperatures not more than 8° or 10° at the most, the mixing of the products causes an immediate fall of 7 or more degrees, the rise then sets in and before long the mixture boils.

There can be no doubt to my mind that the first result in both cases is physical and due to the molecular arrangement between the two liquids, the rise being due to chemical union; it is interesting to get these two changes in the same fluid.

On mixing pure dry ether with aldehyde alone, a fall of temperature occurs, as no chemical compound is formed.

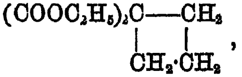
It appears then that aldehyde chemically unites with water, forming ethylidene glycol, the proportions present in the mixture varying with the temperature.

LXXXIV.—*The Synthetical Formation of Closed Carbon-chains. Part I (continued). The Action of Ethylene Bromide on the Sodium-derivatives of Ethylic Acetoacetate, Benzoylacetate, and Acetonedicarboxylate.*

By P. C. Freer, Ph.D., and W. H. Perkin, Jun., Ph.D.

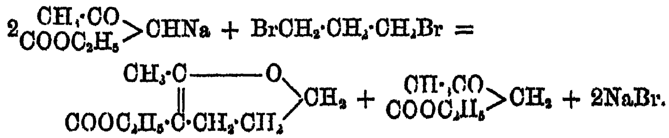
In two papers brought before the notice of the Society by one of us a short time ago (this vol., pp. 1 and 702), the remarkable difference in the behaviour of the sodium-derivatives of ethylic malonate on the one hand and those of ethylic acetoacetate, benzoylacetate, and acetonedicarboxylate on the other hand, towards trimethylene bromide was discussed.

It was shown that in the case of ethylic malonate, a tetramethylene-derivative, that is, ethylic tetramethylenedicarboxylate,



$$\begin{array}{l}(COOC_2H_5)_2C\text{——}CH_2\\ \qquad\quad\; | \qquad\; | \\ \qquad\quad CH_2\cdot CH_2\end{array},$$

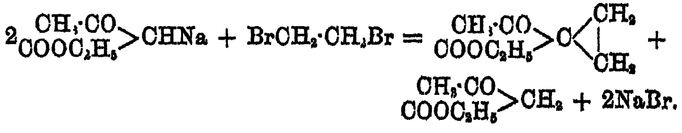
was formed, whereas in the case of ethylic sodacetoacetate, for example, no tetramethylene-derivative was produced, but a reaction took place which is represented by the following equation:—



$$2\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!>\!CHNa + BrCH_2\cdot CH_2\cdot CH_2Br = \begin{matrix}CH_3\cdot C\text{———}O\\ \| \\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\end{matrix}\!>\!CH_2 + \begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!>\!CH_2 + 2NaBr.$$

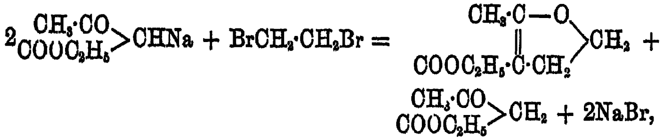
with formation of ethylic methyldehydrohexonecarboxylate.

In a paper published some time since, the results of a series of experiments on the action of ethylene bromide on the sodium compounds of ethylic acetoacetate and benzoylacetate were communicated, and the substances formed in the reaction were assumed to be trimethylene-derivatives. Thus, for example, the reaction between ethylic sodacetoacetate and ethylene bromide was represented as taking place according to the following equation:—



$$2\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!>\!CHNa + BrCH_2\cdot CH_2Br = \begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ | \\ CH_2\end{matrix} + \begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix}\!>\!CH_2 + 2NaBr.$$

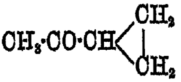
From the results of the experiments on the action of trimethylene bromide on ethylic sodacetoacetate, it was, however, much more likely that the above decomposition would be more correctly represented thus:—



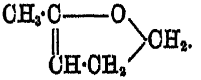
in which case the product would be ethylic methyldehydropentonecarboxylate, and not a derivative of trimethylene as shown in the first equation. This possibility made it necessary to again study this reaction, in the hope of being able to decide whether these compounds really were pentone-derivatives or trimethylene-derivatives.

In experimenting in this direction, a large number of reactions have been studied, most of which can be equally well explained on the assumption of either the trimethylene or the pentone formula, and the only one which has thrown any decisive light on the question is that which takes place when the acid, which has already been described (*loc. cit.*, p. 831) as acetyltrimethylenecarboxylic acid, is distilled. This reaction was mentioned in the previous paper (p. 834), and it is there stated that the acid on distillation is split up into carbonic anhydride, and a colourless oil boiling at 113° (acetyltrimethylene).

As in these experiments only very small quantities of the acid were worked with, and it now appeared that the further study of this substance might throw considerable light on the question of the constitution of the original acid, this decomposition has been restudied, using much larger quantities of the acid. The result has shown that the oil produced in this reaction is a mixture of two substances, the one which is present in by far the larger quantity being the oil boiling at 113°, which was previously noticed, the other, which we have only found in very small quantities, being an oil of ethereal odour boiling at about 90°. The first of these is acetyltrimethylene, the second methyldehydropentone or the anhydride of acetopropyl alcohol. The constitutional formulæ of these two isomeric substances is therefore—

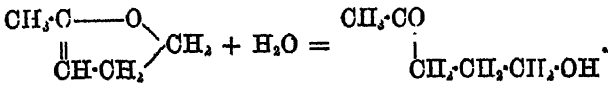


Acetyltrimethylene
(b. p. 113°).



Methyldehydropentone
(b. p. 90° (?)).

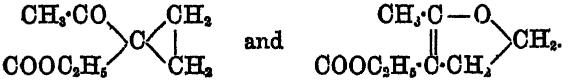
The remarkable difference between these two compounds is seen in their behaviour towards water at ordinary temperatures. Acetyltrimethylene dissolves but remains unchanged, whereas methyldehydropentone is converted into acetopropyl alcohol.



Methyldehydropentone. Acetopropyl alcohol.

The further examination of the properties of acetyltrimethylene has shown that it is a methyl ketone, and is a saturated compound; the only formula therefore which can be assigned to it (at all events according to the system of nomenclature now in use) is the one given above.

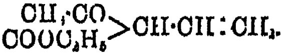
From these results, it follows that the product of the action of ethylene bromide on ethylic sodacetoacetate is a mixture of two substances—ethylic acetyltrimethylenecarboxylate and ethylic methyldehydropentonecarboxylate, which have respectively the following formulæ:—



As the second substance is present in such very small quantities* we propose, for simplicity sake, to treat the product of this reaction in the following paper, as consisting only of ethylic acetyltrimethylenecarboxylate.

We have unfortunately not yet been able to isolate ethylic methyldehydropentonecarboxylate in a state of purity, but we hope, in experimenting further on this subject, to find some means of separating the very small quantity of this substance which is formed in the reaction from the large quantities of ethylic acetyltrimethylenecarboxylate and unchanged ethylic acetoacetate.

The constitution of ethylic acetyltrimethylenecarboxylate, as deduced from the above experiments, is very remarkably supported by the study of its magnetic rotation, and also that of its decomposition products, which has been instituted by my father.

The only constitutional formula possible for ethylic acetyltrimethylenecarboxylate, other than that given above, is that of ethylic vinylacetoacetate,  $\genfrac{}{}{0pt}{}{CH_3\cdot CO}{COOC_2H_5}{>}CH\cdot CH:CH_2$.

Now this differs from ethylic allylacetoacetate in having one CH_2 less than the latter, it therefore follows that the magnetic rotation of ethylic vinylacetoacetate should be that of ethylic allylacetoacetate (10·383) — the value of a CH_2-group (1·023), that is, 9·360. Now the magnetic rotation of the purest sample of ethylic acetyltrimethylenecarboxylate yet examined was found to be 8·198, which shows at once that it cannot be ethylic vinylacetoacetate.

---

* Under some conditions, which we have as yet been unable to determine, it does not appear to be formed at all, a fact which is borne out by the study of the numbers obtained as the magnetic rotation of different samples.

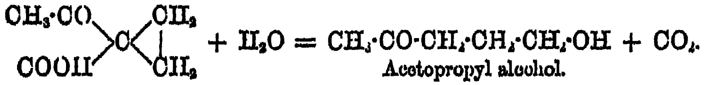
Against the conclusions deduced above from the results of the chemical examination of the products of the distillation of acetyltrimethylenecarboxylic acid, it may be urged that during this reaction some intermolecular change has taken place; that this is not the case, however, the following considerations will show. The magnetic rotation of acetyltrimethylene is 5·245. Now if acetyltrimethylene is really the basis of the original product of the action of ethylene bromide on ethylic sodacetoacetate, it follows that the magnetic rotation of this substance should differ from that of ethylic acetyltrimethylenecarboxylate by the value of ($COOC_2H_5$—H).

The value of this group, as has previously been mentioned (this vol., p. 708), is easily deduced by subtracting the magnetic rotation of acetone from that of ethylic acetoacetate, and is thus found to be 2·987.

If we now add this to the magnetic rotation of acetyltrimethylene, we get as the calculated magnetic rotation of ethylic acetyltrimethylenecarboxylate 8·232, a number which agrees sufficiently with that actually found (8·198), so that at present both the chemical reactions and the physical measurements are in favour of the assumption that these compounds are trimethylene-derivatives.

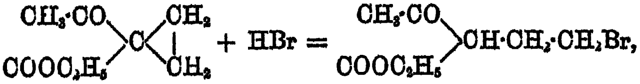
Several other reactions of acetyltrimethylenecarboxylic acid and its ethereal salt have been studied, among which the more important are the following:—

Acetyltrimethylenecarboxylic acid, when boiled with water, is slowly converted into carbonic anhydride and acetopropyl alcohol, thus:—



Acetopropyl alcohol.

Ethylic acetyltrimethylenecarboxylate dissolves easily in a concentrated aqueous solution of hydrogen bromide, being thereby converted into ethylic ω-bromethylacetoacetate:—

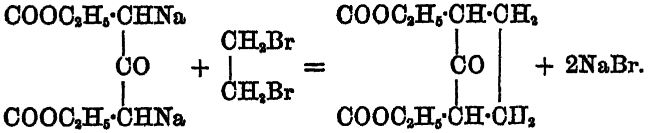


Ethylic ω-bromethylacetoacetate.

a reaction which is a counterpart of the formation of bromethylmalonic acid by the action of hydrogen bromide on trimethylenedicarboxylic acid.

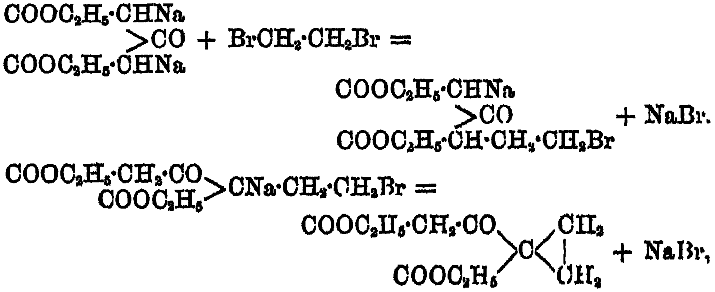
These reactions are undoubtedly difficult to explain on the assumption that these substances are trimethylene-derivatives, as in that case we are bound to assume that by the action of hydrogen bromide, or, more curiously still, by simply boiling with water, the trimethylene-ring is split. At the same time, it must be remembered that the properties of such a ring as the trimethylene-ring are at present totally unknown, and therefore that no definite argument can be drawn from these peculiarities.

While carrying out this research, experiments were also made on the action of ethylene bromide on the disodium-derivative of ethylic acetonedicarboxylate, originally in the hope of obtaining pentamethylene-derivatives, thus :—



$$\begin{array}{l}COOC_2H_5\cdot CHNa\\ \qquad |\\ \qquad CO\\ \qquad |\\ COOC_2H_5\cdot CHNa\end{array} + \begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} = \begin{array}{l}COOC_2H_5\cdot CH\cdot CH_2\\ \qquad |\\ \qquad CO\\ \qquad |\\ COOC_2H_5\cdot CH\cdot CH_2\end{array} + 2NaBr.$$

It was, however, soon discovered that in this case also trimethylene-derivatives were formed, the reaction apparently taking place in the following way :—

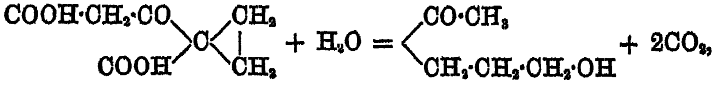


$$\begin{array}{l}COOC_2H_5\cdot CHNa\\ COOC_2H_5\cdot CHNa\end{array}\!\!>\!CO + BrCH_2\cdot CH_2Br = \begin{array}{l}COOC_2H_5\cdot CHNa\\ COOC_2H_5\cdot CH\cdot CH_2\cdot CH_2Br\end{array}\!\!>\!CO + NaBr.$$

$$\begin{array}{r}COOC_2H_5\cdot CH_2\cdot CO\\ COOC_2H_5\end{array}\!\!>\!CNa\cdot CH_2\cdot CH_2Br = \begin{array}{r}COOC_2H_5\cdot CH_2\cdot CO\\ COOC_2H_5\end{array}\!\!>\!C\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + NaBr,$$

the product of the reaction being ethylic acetyltrimethylenedicarboxylate.

The proof of this fact is that on boiling the acid produced by the hydrolysis of this ethereal salt with water, it is decomposed into carbonic anhydride and acetopropyl alcohol, a reaction which is expressed by the following equation :—

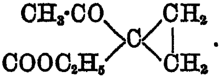


$$\begin{array}{r}COOH\cdot CH_2\cdot CO\\ COOH\end{array}\!\!>\!C\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + H_2O = <\!\begin{array}{l}CO\cdot CH_3\\ CH_2\cdot CH_2\cdot CH_2\cdot OH\end{array} + 2CO_2,$$

a reaction resembling in every respect the formation of acetopropyl alcohol and 1 mol. of carbonic anhydride, from acetyltrimethylenecarboxylic acid, by the action of boiling water.

It is obvious that there are still several points of interest in this research which require more satisfactory explanation, and it is hoped that further experiments which are being carried on will throw some light on these difficulties.

Ethylic Acetyltrimethylenecarboxylate,



In commencing this research, it was necessary in the first place to prepare pure ethylic acetyltrimethylenecarboxylate.

For this purpose, a large quantity of the crude product of the action of ethylene bromide on ethylic sodacetoacetate (prepared as described in a previous paper, Trans., 1885, 829), using, however, 300 grams of ethylic acetoacetate in each experiment, was carefully fractioned, and the fraction 180—210° first separated. This portion was then submitted to most careful fractioning with a long colonna. After repeating this operation about 20 times, an oil was obtained boiling constantly at 195—196°, which gave the following numbers on analysis:—

I. 0·2031 gram substance gave 0·1465 gram H_2O and 0·4565 gram CO_2.

II. 0·1631 gram substance gave 0·1189 gram H_2O and 0·3682 gram CO_2.

	Theory. $C_8H_{12}O_3$.	Found. I.	Found. II.
C	61·54 p. c.	61·30	61·54 p. c.
H	7·69 „	8·01	8·04 „
O	30·77 „	30·69	30·42 „

The determination of the magnetic rotation gave the following numbers:—

$$d\frac{15°}{15°} = 1·05174,$$

$$d\frac{20°}{20°} = 1·04810,$$

$$d\frac{25°}{25°} = 1·04390.$$

Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
19·7°	1·0215	8·471
19·7	1·0175	8·417
19·4	1·0221	8·151
19·4	1·0189	8·425
19·4	1·0201	8·433
18·0	1·0219	8·439
18·0	1·0165	8·395
17·6	1·0233	8·448
17·6	1·0203	8·423
Average 18·7	1·0205	8·434

On still further fractioning this preparation, a product was obtained which boiled at 195—195·5°, and which gave the following numbers:—

Sp. gr. $d\frac{15^\circ}{15^\circ} = 1·05152,$

$d\frac{25^\circ}{25^\circ} = 1·0439.$

Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
15·5°	1·0080	8·310
16·5	1·0120	8·316
Average 16·0	1·0100	8·328

As these numbers were still not so good as might be desired, a specimen of ethylic acetyltrimethylenecarboxylate was prepared from the silver salt of acetyltrimethylenecarboxylic acid by treatment with ethyl iodide. In order to do this, 60 grams of carefully purified acetyltrimethylenecarboxylic acid were dissolved in about five times its weight of water, carefully neutralised with dilute ammonia, and then mixed with a slight excess of a solution of nitrate of silver This caused the precipitation of a very small quantity of silver salt, which was filtered off and discarded.

The clear solution was now evaporated in an open porcelain dish over a free flame as rapidly as possible to about one-third of its bulk, quickly filtered from a small quantity of a black precipitate which always forms, and allowed to stand in a cool place for 12 hours. At the end of this time, it was found that a considerable quantity of silver salt had crystallised out on the bottom of the dish, in the hard greyish-white nodular masses which are so characteristic of this acid. These were collected, well washed with water, and allowed to dry on a porous plate over sulphuric acid in a vacuum. On further evaporation of the mother-liquor, another crop of crystals was obtained, and this operation was continued until no more salt separated.

The dry silver salt thus prepared was then powdered and digested with an excess of ethyl iodide and some pure ether for four hours, at the end of which time the decomposition was complete. The ethereal solution was now filtered from the precipitated iodide of silver, the latter well washed with pure ether, and the ethereal solution evaporated.

In this way, a colourless oil was obtained, which on fractioning boiled constantly at 195·6—196·6°.

Analysis.

0·1793 gram substance gave 0·1304 gram H_2O and 0·4067 gram CO_2.

	Theory. $C_8H_{12}O_3$.	Found.
C	61·54 per cent.	61·76 per cent.
H	7·69 ,,	8·02 ,,
O	30·77 ,,	30·22 ,,

The sp. gr. and magnetic rotation of this preparation gave the following results:—

$$d\frac{15°}{15°} = 1·04703,$$

$$d\frac{25°}{25°} = 1·03930.$$

Magnetic Rotations.

	t.	Sp rotation.	Mol. rotation.
	14·0°	0·9960	8·238
	14·25	0·9975	8·252
	16·5	0·9945	8·241
Average	14·76	0·9960	8·245

This product was then again carefully fractioned and re-examined with the following results:—

$$d\frac{15°}{15°} = 1·04753.$$

Magnetic Rotations.

	t.	Sp. rotation.	Mol rotation.
	15°	0·9873	8·171
	15	0·9913	8·229
	15	0·9903	8·195
Average	15	0·9306	8·198

The value 8·198, which is believed to most nearly represent the true magnetic rotation of ethylic acetyltrimethylenecarboxylate, differs very widely from the number previously published for that substance, namely, 9·817 (Trans., *loc. cit.*, p. 831). The preparation from which this latter value was deduced was specially prepared for the determination of its physical properties by treating a large quantity of the crude product of the action of ethylene bromide on ethylic acetoacetate, boiling at 180—220°, with potash until about three-fourths had been hydrolysed. The remaining oil was then fractioned and found to boil between 197° and 210°. By repeated refractioning a portion was separated boiling between 204° and 206°, which on examination gave the numbers already published. As it was possible that some mistake had been made, the product was re-examined with the following results:—

Magnetic Rotation.

	t.	Sp. rotation.	Mol. rotation.
	12·5°	1·1696	9·865
	12·5	1·1596	9·780
	12·5	1·1643	9·820
	12·5	1·1623	9·802
Average	12·5	1·1630	9·817

The number 9·817 is the same as that obtained in the original measurements.

On refractioning the product, it was found to boil, with the exception of one or two drops at the end, between 204° and 206°. It is at present impossible to understand what this substance was, as even if it had consisted entirely of ethylic methyldehydropentonecarboxylate, the rotation would not have been so high.

Action of Water on Acetyltrimethylenecarboxylic Acid.

Acetyltrimethylenecarboxylic acid when boiled with water is slowly split up into acetopropyl alcohol and carbonic anhydride as mentioned in the introduction.

In preparing acetyltrimethylenecarboxylic acid, it is not necessary to start from the pure ethereal salt or to conduct the hydrolysis at ordinary temperatures. Considerable quantities of this acid have been obtained in the following way. The fraction 180—210° of the crude product of the action of ethylene bromide on ethylic acetoacetate is mixed with twice the calculated quantity of potash, dissolved in methyl alcohol (or pure ethyl alcohol), and boiled for five hours on a water-bath. The alcohol is then distilled off, the product dissolved in water, and evaporated in an open basin on a water-bath till the last traces of alcohol have been expelled. When cool, dilute sulphuric acid is added in excess, and the acid extracted about 10 times with pure ether. The ethereal solution, after drying over calcic chloride and evaporating, deposits the acetyltrimethylenecarboxylic acid as a slightly brownish-coloured oil, which is pure enough for ordinary purposes. If required in a pure state, it is treated as described previously (*loc. cit.*, 832).

To prepare acetopropyl alcohol, the crude acid is dissolved in five times its weight of water, and boiled with reflux condenser until the evolution of carbonic anhydride has ceased, which is usually the case in about 14 hours. If the resulting clear solution, after cooling, is saturated with anhydrous potassic carbonate, the acetopropyl alcohol separates on the surface of the liquid as a brownish-coloured oily layer, which should be extracted at least 20 times with pure ether. The ethereal solution is then dried over carbonate of potash, filtered, and distilled, when the crude alcohol remains behind as a slightly brownish-coloured syrup.

This crude product cannot be purified by distillation under ordinary pressures, as it is to a considerable extent decomposed into water and its anhydride. When rapidly heated under a pressure of 100 mm., however, it distils over between 140° and 150° almost without decomposition. After two distillations, a product was obtained boiling constantly at 144—145°, which gave the following numbers on analysis:—

0·2396 gram substance gave 0·2095 gram H_2O and 0·5174 gram CO_2.

	Theory. $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$.	Found.
C	58·82 per cent.	58·88 per cent.
H	9·81 ,,	9·71 ,,
O	31·37 ,,	31·41 ,,

The determinations of its sp. gr. and magnetic rotation gave the following numbers:—

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}00514,$$

$$d\frac{20^\circ}{20^\circ} = 1{\cdot}00197,$$

$$d\frac{25^\circ}{25^\circ} = 0{\cdot}99896.$$

Magnetic Rotations.

	t	Sp rotation	Mol rotation.
	25°	0·9787	5·552
	25	0·9773	5·543
	25	0·9802	5·560
	25	0·9735	5·522
Average	25	0·9774	5·544

On comparing this value, 5·544, with that previously obtained (Trans., 1887, 719) for acetobutyl alcohol,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = 6{\cdot}502,$$

it will be seen that the difference for the CH_2-group = 0·958, a value closely corresponding with the true value = 1·023; this clearly shows that the constitution of acetopropyl alcohol must be similar to that of acetobutyl alcohol, which is the next member higher in the series The reason why the numbers do not agree exactly is that it was found impossible to obtain acetopropyl alcohol free from its anhydride.

Experiments are in progress with the object of further proving the constitution of acetopropyl alcohol to be that assigned to it above.

Acetopropyl alcohol is a thick, colourless syrup which mixes with water in all proportions. When slowly heated, it is completely decomposed into its anhydride and water, so that the distillate from such an operation is found to consist of two layers, which, however, in a few hours completely amalgamate again with regeneration of acetopropyl alcohol.

Acetopropyl alcohol does not appear to have any action on an ammoniacal solution of silver at the ordinary temperature; on warming the mixture in a water-bath, however, reduction rapidly sets in. It does not reduce Fehling's solution in the cold, and only very slowly on boiling.

If the aqueous solution of acetopropyl alcohol is mixed with a solution of phenylhydrazine hydrochloride in sodic acetate, the phenylhydrazine compound is precipitated as a yellowish oil which was not further examined as it did not crystallise. When boiled with an excess of concentrated nitric acid, acetopropyl alcohol is violently attacked with formation of red fumes. If, however, five drops of the alcohol be mixed with two drops of concentrated nitric acid and gently warmed, an intense pinkish-brown solution is obtained, which is changed to yellow on the addition of alkali. When treated with iodine and potash, acetopropyl alcohol yields iodoform.

Decomposition of Acetyltrimethylenecarboxylic Acid by Heat.

In studying this decomposition, 15 grams of carefully purified acid contained in a small retort connected with a well-cooled condenser was heated gradually to about 200° in a metal bath. At about 120°, rapid decomposition set in, carbonic anhydride was evolved, and a small quantity of a colourless oil together with a little water passed over. On raising the temperature to 200°, the principal product of the reaction distilled, leaving a considerable residue in the retort, which has not been examined, but probably consists of complicated condensation products. From 75 grams of acid treated in this way, 35 grams of crude distillate were obtained. This was carefully fractioned in a Würtz flask with a long neck, when about 14 grams of an oil mixed with a little water distilled over between 65° and 95°. The thermometer then rose rapidly to 135°, a further quantity of 15 grams coming over below this temperature. Above 135°, there was a small residue consisting of high boiling condensation products mixed with a little acetopropyl alcohol.

The fraction 65—95°, after drying over anhydrous potassic carbonate, was refractioned, when it was found that the boiling point had undergone a most remarkable alteration, for now only 4 grams passed over between 85° and 95°, the remainder boiling almost constantly between 112° and 114°.

The fraction 85—95° consists for the most part of the anhydride of acetopropyl alcohol, in a more or less pure state, and in order to prove this, the oil was mixed with twice its weight of water, and allowed to stand at the ordinary temperature; at the end of two days it was found that the oily layer had almost entirely disappeared, it having in fact been converted into acetopropyl alcohol. This was isolated by saturating the liquid, which had previously been carefully freed from oily drops, with potassic carbonate, and extracting several times with ether. On distilling the ethereal solution, after drying it over potassic carbonate, a small quantity of a colourless syrup was obtained, which on standing for a short time over sulphuric acid gave the following numbers on analysis:—

0·1405 gram substance gave 0·1241 gram H_2O and 0·3068 gram CO_2.

	Theory. $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C	58·82 per cent.	59·55 per cent.
H	9·81 „	9·72 „
O	31·37 „	30·73 „

These numbers agree sufficiently well to show that acetopropyl alcohol had been formed, and a further examination of the behaviour of this oil with phenylhydrazine hydrochloride and oxidising agents left no doubt as to its identity.

The portion of the original oil boiling at 95—135° was now re-fractioned; the principal fraction obtained boiled at 110—120°, and weighed 8 grams. This was mixed with the other sample of oil boiling at 112—114°, and the two submitted to three or four careful distillations. In this way, an oil was obtained boiling constantly at 113—114°, which is identical with that of the acetyltrimethylene described by one of us in a previous paper (*loc. cit.*, 835). It was not again analysed.

This substance was also subjected to a physical examination by my father with the following results:—

Sp. gr.

$$d^{15°}_{15°} = 0\ 90471,$$

$$d^{20°}_{20°} = 0·90083,$$

$$d^{25°}_{25°} = 0·89706.$$

Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
23·7°	1·0055	5·225
22 0	1·0138	5·261
22 0	1·0088	5·235
22 0	1 0115	5·249
22·0	1 0133	5·251
22·0	1·0100	5·211
Average 22·3	1·0105	5·245

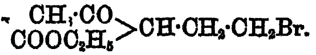
Acetyltrimethylene possesses in every respect the characteristics of a ketone. It dissolves slowly in sodic bisulphite, forming an easily soluble bisulphite compound which, on the addition of alkalis, is decomposed with separation of the original substance. When mixed with phenylhydrazine, a violent reaction sets in, water separates, and an oily phenylhydrazine compound is formed which has not been further examined.

In order to prove that acetyltrimethylene differs very widely from the anhydride of acetopropyl alcohol, 5 grams of the former substance were mixed with 20 grams of water and allowed to stand for six weeks, the whole being shaken up every day. A considerable quantity of the oil dissolved in the water, and it was thought at first that some decomposition had taken place. The whole was therefore extracted with very pure ether, dried over potassic carbonate, and the ether very carefully distilled off. On fractioning the residue, almost the whole quantity passed over between 110° and 120°, only a very small residue remaining which could not be driven over without superheating. Acetyltrimethylene is therefore not the anhydride of a ketone alcohol.

On heating with water for 10 hours at 100—120°, acetyltrimethylene appears to be converted into acetopropyl alcohol, but as this is still doubtful no weight can be laid on the result, and the experiment must be repeated.

Action of Hydrogen Bromide on Ethylic Acetyltrimethylenecarboxylate.

Ethylic ω-Bromethylacetoacetate,



$$\begin{matrix} CH_3\cdot CO \\ COOC_2H_5 \end{matrix}\!>CH\cdot CH_2\cdot CH_2Br.$$

Ethylic acetyltrimethylenecarboxylate combines readily with hydrogen bromide, with evolution of heat and formation of ethylic ω-bromethylacetoacetate, as shown in the introduction, the reaction being parallel to the formation of ethylic ω-bromethyl malonate from ethylic trimethylenedicarboxylate.

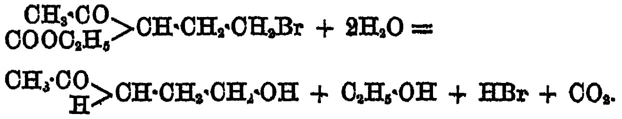
In order to prepare ethylic ω-bromethylacetoacetate, pure ethylic acetyltrimethylenecarboxylate is dissolved in three times its volume of concentrated hydrogen bromide solution (sp. gr. 1·85), the mixture being kept well cooled. After being allowed to stand for about 10 minutes at the ordinary temperature, it is poured into ice-water. This causes the separation of a heavy oil which is extracted from the aqueous solution by means of ether. After washing with water, and drying over calcic chloride, the ether is distilled off, when nearly pure ethylic ω-bromethylacetoacetate remains behind in the form of a heavy oil, of slightly yellowish colour. In order to obtain it in a state fit for analysis, it was allowed to stand for some days over sticks of caustic potash in a vacuum.

A bromine determination gave the following result, which approximately agrees with the formula $C_8H_{13}BrO_3$.

	Theory.	Found.
Br	33·47 per cent.	32·89 per cent.

Ethylic ω-bromethylacetoacetate is a heavy oil, with an odour closely resembling that of camphor. When exposed to the air for any length of time, it becomes discoloured, small quantities of hydrogen bromide being at the same time evolved. It cannot be distilled. When treated with zinc-dust and acetic acid, an oil is obtained which on distillation boils constantly at 195° and appears to be ethylic ethylacetoacetate. It was not analysed.

Ethylic ω-bromethylacetoacetate is completely decomposed when heated with alcoholic potash, uninviting tarry products being formed which could not be purified. Hydrolysis with dilute hydrochloric acid was found however to give interesting results, the bromide splitting up in this way into carbonic anhydride, hydrogen bromide, and acetopropyl alcohol, thus:—



$$\begin{matrix} CH_3{\cdot}CO \\ COOC_2H_5 \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CH_2Br + 2H_2O =$$

$$\begin{matrix} CH_3{\cdot}CO \\ H \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH + C_2H_5{\cdot}OH + HBr + CO_2.$$

Acetopropyl Alcohol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

If a mixture of 20 grams of ethylic ω-bromethylacetoacetate, 5 grams of concentrated hydrogen chloride solution, and 20 grams of water are boiled for about two hours in a flask fitted with a reflux condenser, the oil gradually disappears, forming a greenish solution, which now contains acetopropyl alcohol.

In order to isolate this, the solution is saturated with anhydrous potassic carbonate, when the acetopropyl alcohol rises to the top as a dark-coloured layer, which is repeatedly extracted with ether. After drying over potassium carbonate and distilling off the ether, the crude product remains behind as a dark-brown oil. This method of preparation was the first used to obtain acetopropyl alcohol, and on trying to purify the crude product for analysis, as in the case of acetobutyl alcohol, by fractioning under the ordinary pressure, and afterwards under reduced pressure (300 mm.), it was found that the decomposition which set in was considerable, and it was not till later that we succeeded in purifying acetopropyl alcohol, by fractioning under 100 mm. pressure as described on page 829.

The method first used for preparing acetopropyl alcohol for analysis was the following:—

The crude alcohol was mixed with about five times its weight of water, filtered, and the solution extracted once or twice with pure ether, which dissolved out] all the impurities, while the greater part of the acetopropyl alcohol remained behind.

In order to isolate this, it is necessary to saturate the solution with anhydrous potassic carbonate, and to extract at least 10 times with pure ether. After drying over potassic carbonate and distilling off the ether, nearly pure acetopropyl alcohol remains behind in the flask as an almost colourless oil. By repeating this process, a product was obtained, which on analysis gave the following numbers:—

0·1909 gram substance gave 0·1670 gram H_2O and 0·4172 gram CO_2.

	Theory. $C_5H_{10}O_2$.	Found.
C	58·82 per cent.	59·57 per cent.
H	9·81 „	9·83 „
O	31·37 „	30·60 „

A similar process of purification was also first applied to the acetopropyl alcohol obtained from acetyltrimethylenecarboxylic acid by boiling it with water, as described on p. 829.

The analytical results obtained in this case were the following:—

I. 0·1963 gram substance gave 0·1714 gram H_2O and 0·4249 gram CO_2.

II. 0·0736 gram substance gave 0·0643 gram H_2O and 0·1590 gram CO_2.

	Theory. $C_5H_{10}O_2$.	Found. I.	 II.
C	58·82 per cent.	59·04	58·92 per cent.
H	9·81 „	9·70	9·71 „
O	31·37 „	31·26	31·37 „

Acetopropyl alcohol obtained from ethylic ω-bromethylacetoacetate shows all the reactions of that obtained from acetyltrimethylenecarboxylic acid by boiling with water.

Unfortunately, we neglected determining the boiling point of the former, so as to prove the identity of the two products; but as the preparation of acetopropyl alcohol from acetyltrimethylenecarboxylic acid is so much more satisfactory, we have not had occasion to repeat the experiment with ethylic ω-bromethylacetoacetate.

γ-*Pentylene Glycol*, $CH_3\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.

Acetobutyl alcohol, when treated with sodium amalgam, is easily reduced to the corresponding δ-hexylene glycol, as Lipp has shown (*Ber.*, 18, 3282). It therefore seemed probable that acetopropyl alcohol, when subjected to similar treatment, would be converted into γ-pentylene glycol, a substance which would be of great value for the further synthesis of ring derivatives.

If acetopropyl alcohol (10 grams) be diluted with about 5 parts of water, and the theoretical quantity of sodium amalgam (3 per cent. Na) be slowly added to this solution, reduction sets in immediately without evolution of gas, the liquid becoming quite warm. A small quantity of resinous matter, which usually separates during the reduction, is removed by filtration, the colourless filtrate saturated with an excess of anhydrous carbonate of potash, and then repeatedly extracted with ether. After drying over potassium carbonate and distilling off the ether, γ-pentylene glycol remains behind in a nearly pure state. On rapid fractional distillation, the greater part distils over between 210—220° as a colourless oil. This operation must be rapidly accomplished, otherwise a considerable quantity of the glycol is decomposed into water and its anhydride; owing to this fact, it was very difficult to obtain a specimen of γ-pentylene glycol sufficiently pure for analysis.

The best analytical numbers were obtained from a portion which was very rapidly distilled, and then as nearly as possible freed from anhydride and water by passing a stream of dry hydrogen through the liquid for some hours. The following results were then obtained:—

0·1167 gram substance gave 0·1179 gram H_2O and 0·2485 gram CO_2.

	Theory. $C_5H_{12}O_2$.	Found.
C	57·69 per cent.	58·07 per cent.
H	11·54 „	11·21 „
O	30·77 „	30·72 „

At some future date, should we be again in possession of this glycol, it is intended to purify it by rapid distillation in a vacuum.

γ-Pentylene glycol is a thick colourless inodorous syrup, which mixes with water in all proportions. If it be heated in a small retort for some time to its boiling point, water and a very volatile oil distil over, the glycol being in course of time apparently completely decomposed.

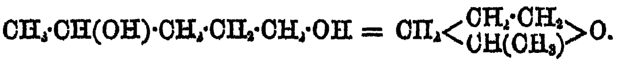
The decomposition into anhydride and water is much more readily accomplished by means of sulphuric acid (compare Lipp, *Ber.*, 18, 3282). If γ-pentylene glycol is heated with 50 per cent. sulphuric acid on a water bath for some time, the anhydride distils over as a very volatile oil of ethereal smell. This when purified was found to boil at 78—83°.

An analysis gave the following result:—

0·1001 gram substance gave 0·1040 gram H_2O and 0·2547 gram CO_2.

	Theory. $C_5H_{10}O$.	Found.
C	69·77 per cent.	69·42 per cent.
H	11·62 „	11·55 „
O	18·61 „	19·03 „

This anhydride is formed from γ-pentylene glycol by the abstraction of the elements of water, thus:—



$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH(CH_3)\end{matrix}{>}O.$$

Action of Water on Benzoyltrimethylenecarboxylic Acid.

After the results obtained in studying the action of water on acetyltrimethylenecarboxylic acid, when, as was shown in a previous chapter, decomposition into carbonic anhydride and acetylpropyl alcohol takes place, it was thought that it would be interesting to experiment on the behaviour of benzoyltrimethylenecarboxylic acid under similar conditions.

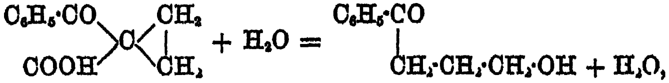
In order to do this, it was necessary in the first place to obtain the acid in as finely divided a condition as possible. This was done by dissolving it (1 gram was used) in dilute ammonia (*vide* this vol., p. 733), and then carefully reprecipitating with dilute sulphuric acid. The fine powder thus obtained was well washed and heated in a sealed tube with 40 c.c. of water at 100—110° for four or five hours, during which time (but more especially at first) the tube was frequently taken out and well agitated to ensure the acid dissolving in the water. On opening the tube, a small amount of carbonic anhydride escaped, and the contents were found to consist of an almost colourless liquid, in which a few small drops of a slightly brownish oil were swimming about. In order to get rid of these, the liquid was filtered several times through wet filter-paper, and the perfectly clear filtrate, after mixing with a little potassic carbonate, was then extracted five times with perfectly pure ether. The ethereal solution, after drying over potassic carbonate and filtering, was evaporated, first on a water-bath to a small bulk, and lastly on a watch-glass. In this way, a colourless oil of aromatic odour was obtained, which, however, was now almost insoluble even in boiling water. After standing in a vacuum over sulphuric acid for four days, an analysis was made with the following result:—

0·1211 gram substance gave 0·0771 gram H_2O and 0·3620 gram CO_2.

	Theory. $C_{10}H_{10}O$.	Found.
C	82·19 per cent.	81·52 per cent.
H	6·85 „	7·06 „
O	10·95 „	11·42 „

This substance is therefore not benzoylpropyl alcohol, $C_{10}H_{12}O_2$, as was expected, but its anhydride.

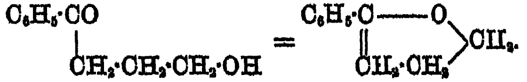
In this decomposition, it is evident that the first reaction which takes place is the following:—



Benzoyltrimethylenecarboxylic acid. Benzoylpropyl alcohol.

a solution of benzoylpropyl alcohol resulting.

That a ketone alcohol is present is easily shown by adding to the clear aqueous solution a solution of phenylhydrazine acetate, when an oily phenylhydrazine compound is at once precipitated. On extracting the solution of this ketone alcohol with ether, drying over potassic carbonate, and distilling off the ether, this unstable substance is apparently at once split up into its anhydride and water, thus:—

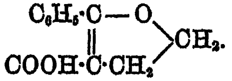


The instability of these aromatic ketone alcohols is very remarkable.

In a previous paper (this vol., p. 718), it was shown that acetobutyl alcohol, when rapidly heated, can be distilled with hardly any appreciable decomposition, whereas the corresponding aromatic alcohol, benzoylbutyl alcohol, (*ibid.*, p. 733) on simply standing over sulphuric acid in a vacuum for some days, is converted into its anhydride and water. The present case is however still more remarkable. Acetopropyl alcohol, although not so stable as acetobutyl alcohol, can still be distilled without appreciable decomposition under a pressure of 100 mm., whereas benzoylpropyl alcohol only appears to exist in solution, and on isolation is at once converted into its anhydride.

It is intended to further examine these interesting alcohols in order to be certain of these points, using larger quantities of material. One interesting point will be to determine whether the anhydride of benzoylpropyl alcohol is or is not identical with benzoyltrimethylene (Trans., 47, 840).

It seems almost probable that if these anhydride rings are so easily formed in the aromatic series, that the derivatives obtained from ethylic benzoylacetate and ethylene bromide are pentone- and not trimethylene-derivatives, in which case the acid described as benzoyltrimethylenecarboxylic acid would be benzoyldehydropentonecarboxylic acid,



Further experiments must decide this point.

Action of Phenylhydrazine on Ethylic Acetyltrimethylenecarboxylate.

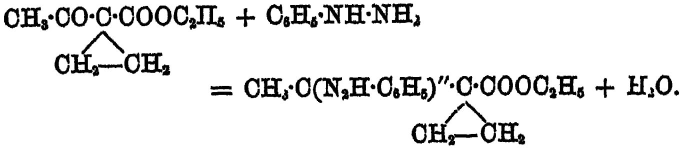
In order to prove the presence of a carbonyl-group in ethylic acetyltrimethylenecarboxylate, several experiments on the action of phenylhydrazine on this substance were made. If the pure ethereal salt is mixed with phenylhydrazine and warmed on a water-bath, a violent reaction sets in with separation of water and formation of a thick yellowish syrup, which even on long standing does not crystallise. On modifying the method slightly in the following way, better results were afterwards obtained. 5 grams of pure ethylic acetyltrimethylenecarboxylate was mixed with a little less than the theoretical quantity of phenylhydrazine (3·3 grams), the mixture heated on a water-bath until all action had ceased, and then submitted to distillation with steam in order to drive over any unchanged ethereal salt. If this product is allowed to stand for some weeks under water, crystals begin to radiate from various points on the bottom of the flask, and at last the oily mass completely solidifies, the whole presenting an appearance somewhat resembling that of cinnamic acid which has been fused and then allowed to cool slowly.

The phenylhydrazine compound thus obtained was broken away from the glass, dried over sulphuric acid in a vacuum, and then treated with various solvents, in the hope of purifying it by recrystallisation. The substance is very easily soluble in nearly all the usual solvents, and all attempts to obtain anything crystalline from these various solutions were unfortunately fruitless. An analysis of the crude substance was therefore made with the following result:—

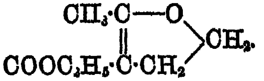
0·2460 gram substance gave 26·0 c.c. N. $t = 19°$. Bar. = 760 mm.

	Theory. $C_{14}H_{18}N_2O_2$.	Found.
N..........	11·38 per cent.	12·38 per cent.

Although these numbers of course are only approximate, still they would appear to show that ethylic acetyltrimethylenecarboxylate reacts with phenylhydrazine in the same way as all substances containing the carbonyl-group, and that the above substance is formed according to the equation—



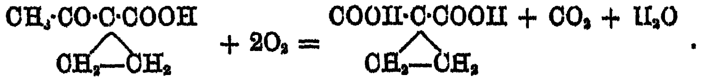
This would then be an additional proof that ethylic acetyltrimethylenecarboxylate is really an acetyltrimethylene-derivative, and does not contain an oxygen carbon-chain, as it would if its constitution were represented by the formula—



From the study of the action of phenylhydrazine on ethylic methyldehydrohexonecarboxylate, it is very improbable that a pentone ring would react with phenylhydrazine.

Oxidation of Ethylic Acetyltrimethylenecarboxylate.

During the course of these experiments, it appeared interesting to experiment on the action of oxidising agents on acetyltrimethylenecarboxylic acid or its ethereal salt, as it seemed possible that in this way trimethylenedicarboxylic acid (1, 1) might be produced, thus:—



In the experiments to be described, ethylic acetyltrimethylenecarboxylate was usually employed.

1. *Oxidation with Chromic Acid.*—The pure ethereal salt was treated with an excess of chromic acid and dilute sulphuric acid. The oxidation sets in rapidly and was hastened at the last by gently warming the mixture. The product was then separated from chromium in the usual way, by precipitating with caustic soda, the alkaline filtrate boiled to hydrolyse any ethereal salt that might be present, acidified and several times extracted with ether. On distilling off the ether, a slight residue was obtained which, however, did not contain any trimethylenedicarboxylic acid. These experiments were then repeated with only sufficient chromic acid to oxidise the methyl-group in the

ethylic acetyltrimethylenecarboxylate to the carboxyl-group, but it was found that in this case part of the ethereal salt had been completely destroyed, leaving the greater part quite unchanged.

2. *Oxidation with Potassic Permanganate.*—In these experiments the ethereal salt was first strongly agitated with dilute sodium carbonate solution, until a fine emulsion was formed, and then the calculated quantity of permanganate of potassium solution was slowly run in. The colour of the permanganate disappears instantly at first, but more slowly towards the end of the operation. After filtering from the precipitated manganese oxide, a little caustic soda was added, the solution boiled for some time, evaporated, acidified and repeatedly extracted with ether. On distilling off the ether, an uninviting brown substance remained behind, from which nothing but acetic acid could be extracted. There was no trimethylenedicarboxylic acid present.

3. *Oxidation with Iodine in Alkaline Solution.*—As it was thought possible that weaker oxidising agents than chromic acid and permanganate might yield better results, several experiments were made with iodine in alkaline solution. As in the previous experiment, an emulsion of the ethereal salt with dilute sodic carbonate solution was first prepared, and then treated with a little less than the calculated quantity of iodine. As soon as all the iodine had been added, any excess of ethereal salt was removed by extracting with ether, the aqueous solution was then acidified, and again several times extracted with ether. On distilling off the ether, a very small residue was obtained which evidently did not contain any trimethylenedicarboxylic acid. The principal products of the reaction were iodoform and considerable quantities of oxalic acid.

These oxidation experiments were repeated several times, not only with the ethereal salt but also with the free acid, but in no case could trimethylenedicarboxylic acid be obtained.

Action of Phosphorous Pentachloride on Ethylic Acetyltrimethylenecarboxylate.

In this experiment, 50 grams of the crude ethereal salt, boiling at 190—200°, were dissolved in twice the volume of chloroform, and to this 67 grams of phosphorus pentachloride were slowly added. The action was very violent, so that it was found necessary to cool the mixture with ice-water after each addition of the pentachloride, otherwise resinous substances are apt to be formed. After standing 24 hours to ensure the completion of the reaction, the mass was gradually poured inco ice and water, and then as soon as all the oxychloride and excess of pentachloride of phosphorus had been decomposed, the oil was extracted with ether. The ethereal solution was well washed, first with water and then with dilute carbonate of soda, dried over calcic chloride, filtered, and the other distilled off; the yellowish oil which remained behind was purified by fractioning under diminished pressure (150 mm.). After repeated fractioning, an oil was obtained boiling constantly at 171—173° (150 mm.); this was analysed with the following result:—

	Theory. $C_8H_{12}O_2Cl_2$.	Found.
Cl......	33·65 per cent.	28·90 per cent.

On each fractioning, it was noticed that traces of gaseous hydrogen chloride were always given off; the experiments were therefore repeated, and the resulting oil now fractioned under a pressure of only 35 mm. The portion boiling at 135—140° gave the following analytical numbers:—

I. 0·2180 gram substance gave 0·1194 gram H_2O and 0·3629 gram CO_2; 0·4405 gram substance gave 0·5430 gram AgCl.

II. 0·2174 gram substance gave 0·1132 gram H_2O and 0·3598 gram CO_2; 0·2188 gram substance gave 0·2885 gram AgCl.

III. 0·3200 gram substance gave 0·4178 gram AgCl.

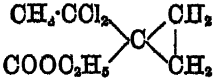
	Theory. $C_8H_{12}O_2Cl_2$.	Found. I.	 II.	 III.	
C	45·40 p. c.	45·40	45·15	—	p. c.
H	5·68 „	6·08	5·78	—	„
Cl	33·65 „	30·57	32·71	32·39	„

Even under a pressure of only 35 mm., it is not possible to distil this oil without traces of hydrogen chloride being given off, and this accounts for the chlorine determinations in the above analyses not agreeing so well as might be desired.

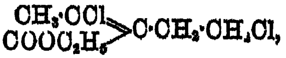
This chlorinated compound is a colourless oil, of powerful odour, which on standing soon becomes yellowish. When pure, it distils with only slight decomposition at ordinary temperatures.

There are two possible formulæ for this substance—

I.



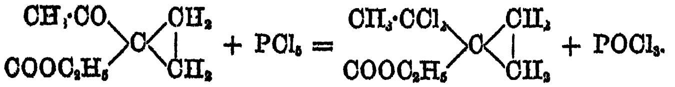
II.



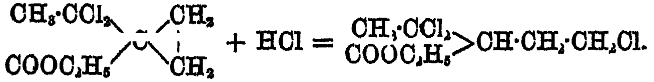
$$\begin{matrix}CH_3\cdot CCl\\ COOC_2H_5\end{matrix}\!>C\cdot CH_2\cdot CH_2Cl,$$

of which the second is certainly the most plausible.

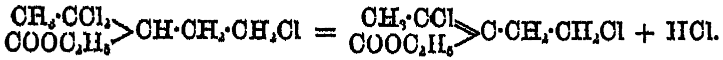
The most probable explanation of the action of pentachloride of phosphorus on ethylic acetyltrimethylenecarboxylate is that a substance having the constitution represented by Formula I is first formed according to the equation—



This substance is then further acted on by hydrogen chloride, which is always present; the trimethylene-ring is split, and a change takes place which may be represented by the following equation:—



This intermediary compound then loses 1 mol. HCl probably during the reaction, but certainly on distillation, when a substance results which would have the constitution represented by Formula II; thus:—



$$\begin{matrix}CH_3\cdot CCl_2\\COOC_2H_5\end{matrix}>CH\cdot CH_2\cdot CH_2Cl = \begin{matrix}CH_3\cdot CCl\\COOC_2H_5\end{matrix}>C\cdot CH_2\cdot CH_2Cl + HCl.$$

The hydrogen chloride thus produced could then react with a further quantity of the original chlorinated compound, and thus a continuous reaction would be set up.

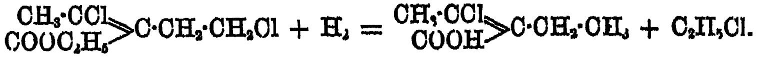
The examination of the behaviour of this substance, for which we would suggest the name ethylic chlorethylchlorocrotonate, towards reducing agents has tended to confirm the above speculations. When a boiling alcoholic solution of ethylic chlorethylchlorocrotonate is treated with an excess of zinc-dust and concentrated hydrochloric acid, reduction and partial hydrolysis sets in. If the product is diluted with water, an oil is deposited, which may be separated from the aqueous layer by extraction with ether. This oil, on examination, was found to consist of an acid and a neutral substance. In order to separate these, the ethereal solution was shaken up with a slight excess of sodic carbonate, the alkaline layer separated, acidified with dilute sulphuric acid, and then allowed to stand in a cool place. After a short time a small quantity of a colourless substance crystallised out, which was filtered from the mother-liquor, washed with a little water, and dried over sulphuric acid in a vacuum. The amount of this substance, which was found to contain chlorine, was only 0·3 gram.

A determination of the chlorine gave the following result:—

0·1936 gram substance gave 0·1801 gram AgCl.

	Theory. $CH_3\cdot CCl : C(C_2H_5)\cdot COOH$.	Found.
Cl........	23·90 per cent.	23·00 per cent.

These numbers agree approximately with the formula of chlorethylcrotonic acid, a substance which has been obtained by Demarçay by treating ethylic ethylacetoacetate with pentachloride of phosphorus. Demarçay found the melting point of his substance to be 74—75°. The crystals obtained by us melted at almost the same temperature, so that it is extremely probable that the two products are identical. The formation of chlorethylcrotonic acid from ethylic chlorethylchlorocrotonate can be easily explained by the following equation:—



$$\begin{matrix}CH_3\cdot CCl\\ COOC_2H_5\end{matrix}\!>\!C\cdot CH_2\cdot CH_2Cl + H_2 = \begin{matrix}CH_3\cdot CCl\\ COOH\end{matrix}\!>\!C\cdot CH_2\cdot CH_3 + C_2H_5Cl.$$

It is unfortunate that the amount of substance at our disposal was not sufficient to admit of a complete analysis, and thus prove the formula conclusively. We, however, intend to repeat these experiments at some future date with larger quantities of material. The neutral oil formed by the reduction of ethylic chlorethylchlorocrotonate, which was separated from the chlorethylcrotonic acid as described above, has also not yet been further examined.

Experiments were next tried on the action of sodium amalgam on ethylic chlorethylchlorocrotonate. For this purpose, the pure ethereal salt was dissolved in 80 per cent. alcohol and treated with a large excess of 3 per cent. sodium amalgam, the reaction at the last being accelerated by gently warming on a water-bath. On diluting the mass with water, only a very small quantity of oil was precipitated, showing that, as was expected, hydrolysis of the reduced product had also taken place. The neutral oil was removed by shaking with a little ether, the alkaline liquid acidified with sulphuric acid, and several times extracted with pure ether. The ethereal solution, after drying and evaporating, deposited a considerable quantity of a putrid smelling oil, which, on fractioning, all distilled between 185° and 205°.

On refractioning this, an oil was obtained boiling between 195° and 200°, which gave the following numbers on analysis:—

0·1812 gram substance gave 0·1721 gram H_2O and 0·4106 gram CO_2.

	Theory. $(C_2H_5)_2CH\cdot COOH$.	Found.
C.....	62·07 per cent.	61·75 per cent.
H.....	10·34 „	10·55 „
O	27·59 „	27·70 „

This substance appears therefore to be diethylacetic acid. This acid has already been prepared in several ways, and its boiling point has been determined as 190° (755 mm., Fittig), and 195—197° (Schnapp), temperatures which correspond sufficiently closely with that obtained for our product.

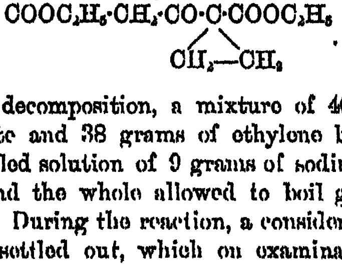
The formation of diethylacetic acid from ethylic chlorethylchlorocrotonate takes place according to the equation—

$$\begin{matrix}CH_3\cdot CCl\\COOC_2H_5\end{matrix}\!\!>C\cdot CH_2\cdot CH_2Cl + 2H_2 + H_2O = \begin{matrix}CH_3\cdot CH_2\\COOH\end{matrix}\!\!>CH\cdot CH_2\cdot CH_3 + C_2H_5\cdot OH + 2HCl.$$

When treated with hydriodic acid, ethylic chlorethylchlorocrotonate undergoes a similar reduction. 3 grams of the pure ethereal salt, 10 c.c. of fuming hydriodic acid, and 1 gram of amorphous phosphorus were heated in a sealed tube for four hours at 200°. The product from three such tubes was neutralised with sodic carbonate, freed from ethyl iodide by distillation in steam, and the residue extracted with ether, to remove any unchanged oil. The alkaline solution was then acidified, and several times extracted with ether. The ethereal solution, after drying and evaporating, deposited a colourless oil, which on fractioning distilled between 180° and 200°, and on repeating the operation, by far the greater part came over between 190° and 195°, and possessed all the properties of diethylacetic acid.

Action of Ethylene Bromide on Ethylic Acetonedicarboxylate.

Ethylic Acetyltrimethylenedicarboxylate,



$$COOC_2H_5\cdot CH_2\cdot CO\cdot \underset{CH_2-CH_2}{C}\cdot COOC_2H_5$$

In studying this decomposition, a mixture of 40 grams of ethylic acetonedicarboxylate and 38 grams of ethylene bromide was slowly added to a well-cooled solution of 9 grams of sodium in 100 grams of absolute alcohol, and the whole allowed to boil gently on a water-bath for 10 hours. During the reaction, a considerable quantity of a white precipitate settled out, which on examination was found to contain not only bromide of sodium, but also a considerable quantity of carbonate. In order to isolate the principal product of the reaction, the excess of alcohol was distilled off, the residue mixed with water, and the resulting oil extracted several times with ether. The ethereal solution after well washing, drying over calcic chloride, and distilling, deposited about 30 grams of a yellowish oil, which was then submitted to distillation, at first under the ordinary pressure, till the thermometer had risen to 180°, when the distillation was continued under reduced pressure (150 mm.).

Below 100°, a considerable quantity of a colourless oil distilled over, which on examination was found to consist for the most part of ethylic acetoacetate, produced by the partial hydrolysis of some of the ethylic acetonedicarboxylate, together with a little ethylene bromide.

The oil distilled under reduced pressure (150 mm.) boiled for the most part between 130° and 240°, and this on refractioning split up into two principal fractions, 130—200° and 200—240°. The second of these, which contains the primary product of the action of ethylene bromide on ethylic acetonedicarboxylate, was several times very carefully fractioned under the same pressure (150 mm.), when the pure substance was at last obtained as a very thick, almost colourless oil, boiling at 223—224° (150 mm). Analyses showed this to be *ethylic acetyltrimethylenedicarboxylate.*

I. 0·1686 gram substance gave 0·1120 gram H_2O and 0·3590 gram CO_2.

II. 0·1962 gram substance gave 0·1286 gram H_2O and 0·4180 gram CO_2.

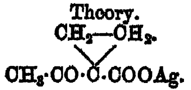
	Theory. $C_{11}H_{16}O_5$.	Found. I.	Found. II.
C	57·89 p. c.	58·07	58·13 p. c.
H	7·02 „	7·38	7·28 „
O	35·09 „	34·55	34·59 „

Ethylic acetyltrimethylenedicarboxylate when freshly distilled is an almost colourless syrup, of a peculiar odour, somewhat resembling that of pyruvic acid. It is a very unstable substance, a fact which probably accounts for the smallness of the yield obtained in the above reaction (about 10 per cent. of the theoretical). It combines with phenylhydrazine, and in alcoholic solution gives a violet coloration with ferric chloride.

The fraction 130—200° (150 mm.), which is always formed in considerable quantity in the above reaction, was next carefully fractioned under the ordinary pressure. After two or three distillations, by far the greater part passed over between 185° and 200°, and on examination proved to be ethylic acetyltrimethylenecarboxylate. It was not directly analysed, but converted by hydrolysis into the corresponding acid, and this into its silver salt (as described on p. 848). The silver salt, after twice recrystallising from water, was obtained in the characteristic form already described (*loc. cit.*, p. 833). An analysis gave the following numbers, showing it to be argentic acetyltrimethylenecarboxylate.

0·2433 gram substance gave 0·1112 gram Ag.

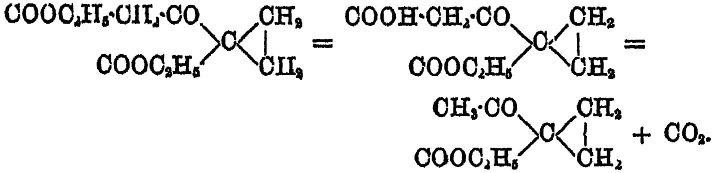
Theory.

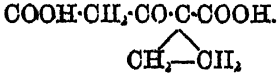


$CH_3\cdot CO\cdot\overset{CH_2—CH_2}{C}\cdot COOAg$.

	Theory.	Found.
Ag	45·97 per cent.	45·70 per cent.

Ethylic acetyltrimethylenecarboxylate is produced from ethylic acetyltrimethylenedicarboxylate, by partial hydrolysis and subsequent splitting off of carbonic anhydride, thus:—



Acetyltrimethylenedicarboxylic Acid, 

In preparing acetyltrimethylenedicarboxylic acid from its ethereal salt, considerable difficulty was experienced owing to the instability of the acid, and it was only after several experiments had been made, that small quantities of this substance were obtained in a fairly pure condition.

The following method was at length found to give the best results:—Pure ethylic acetyltrimethylenedicarboxylate was mixed with a strong solution of twice the calculated quantity of pure potash in methyl alcohol, and the resulting yellow solution allowed to stand at the ordinary temperature for about 12 days. The product was then diluted with water, acidified with dilute sulphuric acid, and several times extracted with ether. The yellowish-coloured ethereal solution after well washing with water, drying over calcic chloride and distilling, deposited a dark-yellowish oil, which almost entirely solidified on standing for some days over sulphuric acid in a vacuum.

This crude substance was next roughly separated from mother-liquor by spreading it out on a porous plate, and allowing it to remain for several days; it was then broken up and washed with small quantities of chloroform, until all the impure mother-liquor had been dissolved out, leaving a white crystalline solid. This is nearly pure acetyltrimethylenedicarboxylic acid.

Analysis.

I. 0·1796 gram substance gave 0·0791 gram H_2O and 0·3188 gram CO_2.

II. 0·1540 gram substance gave 0·0670 gram H_2O and 0·2723 gram CO_2.

	Theory. $C_7H_8O_5$.	Found. I.	Found. II.
C........	48·83 p. c.	48·41	48·22 p. c.
H........	4·65 „	4·89	4·83 „
O........	46·52 „	46·70	46·95 „

Acetyltrimethylenedicarboxylic acid melts at about 175° with decomposition into carbonic anhydride and an oil of ethereal odour, probably acetyltrimethylene. It is easily soluble in most of the usual solvents, with the exception of water and chloroform, in which it dissolves sparingly at the ordinary temperature.

The silver salt of this acid was prepared by dissolving the acid in a slight excess of ammonia, allowing the solution to stand over sulphuric acid in a vacuum until neutral, and then precipitating with nitrate of silver. It is a white amorphous mass, sparingly soluble in water. For analysis, it was collected on a filter, well washed with water, and dried over sulphuric acid in a vacuum. A combustion of this salt gave the following results:—

0·2157 gram substance gave 0·0354 gram H_2O; 0·1767 gram CO_2; Ag was lost.

	Theory. $C_7H_6O_5Ag_2$.	Found.
C........	22·70 per cent.	22·34 per cent.
H........	1·62 „	1·82 „
Ag	58·38 „	—

When heated in a combustion tube, the silver salt decomposes all at once as soon as the temperature reaches a certain point, with evolution of a considerable quantity of gas, and deposition of a voluminous mass of fine threads of silver, which cling to the top of the tube, and thus prevented the estimation of the silver in the above analysis. Owing to lack of material, we were unfortunately not able to repeat this determination.

In order to show more clearly the relation of acetyltrimethylenedicarboxylic acid to the monocarboxylic acid, the action of water on the former was also studied, and it was found that this acid, on boiling with water, was split up into acetopropyl alcohol and 2 mols. of carbonic anhydride, in the same way that acetyltrimethylenemonocarboxylic acid, under similar treatment, yields acetopropyl alcohol and 1 mol. of carbonic anhydride.

The experiment was carried out as follows:—2 grams of the pure acid were dissolved in a small quantity of hot water, and the solution thus obtained boiled with a reflux condenser until the evolution of carbonic anhydride had ceased. Excess of potassic carbonate was then added, and the resulting milky liquid extracted about 20 times with small quantities of ether. The ethereal solution was then dried over potassic carbonate, filtered and evaporated, when a considerable quantity of a thick colourless oil was obtained, which showed all the properties of acetopropyl alcohol. After allowing it to stand for a short time over sulphuric acid in a vacuum, it was analysed with the following result:—

0·1128 gram substance gave 0·1027 gram H_2O and 0·2415 gram CO_2

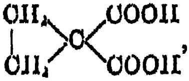
	Theory. $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C	58·82 per cent.	58·39 per cent.
H	9·81 „	10·16 „
O	31 37 „	31·45 „

This result clearly shows that the substances described above, as produced by the action of ethylene bromide on ethylic acetonedicarboxylate, are really derivatives of acetyltrimethylenecarboxylic acid.

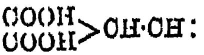
This research was carried out partly at Prof. v. Baeyer's laboratory in Munich, and partly at Prof. Dixon's private laboratory at Owens College, Manchester.

LXXXV.—*The Synthetical Formation of Closed Carbon-chains.* Part I (continued). *Trimethylenedicarboxylic Acid.*

By W. H. Perkin, Jun., Ph.D.

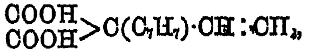
In the previous paper on trimethylene-derivatives (Trans., **47**, 818), among other substances an acid was described under the name of trimethylenedicarboxylic acid, which for several reasons was supposed to have the constitution , and to be a true trimethylene-derivative.

As was shown in this paper, it was not necessary that this acid should have this formula; it is perfectly possible to assume that in this reaction an unsaturated compound had been formed, such as that represented by the formula—



$$\begin{matrix}COOH\\COOH\end{matrix}>CH\cdot CH:CH_2$$ (*i.e.*, vinylmalonic acid).

One of the grounds given as being greatly in favour of the trimethylene formula was that the ethereal salt of this acid when treated with benzyl chloride and sodium ethylate did not give the ethereal salt of benzyl vinylmalonic acid—



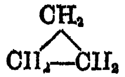
$$\begin{matrix}COOH\\COOH\end{matrix}\!>\!C(C_7H_7){\cdot}CH{:}CH_2,$$

which it should have done had it been simply a mono-substituted ethyl malonate.

Fittig and Marburg (*Ber.*, 18, 3414) have since doubted the value of this proof, because in carrying out the experiment I mixed the ethylic trimethylenedicarboxylate first with the benzyl chloride, and then added the sodium ethylate, which of course admits of the possibility of the sodium ethylate acting on the benzyl chloride at once, before any sodium compound of the ethylic trimethylenedicarboxylate had been formed.

In order to clear up this point, I have repeated this experiment in the following way:—14 grams of ethylic trimethylenedicarboxylate was first carefully added to a cold solution of 1·8 grams of sodium dissolved in 20 grams of absolute alcohol, and after the mixture had stood for about two minutes it was treated with 9·5 grams of benzyl chloride and heated to boiling on a water-bath for about an hour, at the end of which time the product showed neutral reaction. Water was then added, the precipitated oil extracted twice or thrice with ether, the ethereal solution washed with water, dried over calcic chloride, and the ether distilled off.

The residue on fractioning distilled over almost entirely between 175° and 220°, leaving only a very small residue behind. There had evidently been no ethylic benzyl vinylmalonate formed, as a substance of that constitution would have a much higher boiling point. On submitting this fraction to hydrolysis, it split up into trimethylenedicarboxylic acid and benzyl ethyl ether, $C_6H_5{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, the amount of the latter which was present being almost that which should have been formed had all the benzyl chloride reacted simply with the sodic ethylate. It is therefore clear that ethylic trimethylenedicarboxylate, as before stated, does not form a sodium compound when treated with sodium ethylate. Fittig and Marburg also state that I, in my previous publication, laid great stress on the fact that vinaconic acid (trimethylenedicarboxylic acid) did not combine with bromine as supporting the view that the acid was a trimethylene-derivative. This, however, is not so. Freund (*Monatshefte*, 1882, 625) has shown in his experiments on trimethylene that this gas is acted on by bromine, though very slowly, trimethylene bromide being formed—



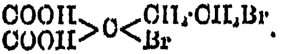
$$+ Br_2 = CH_2Br{\cdot}CH_2{\cdot}CH_2Br.$$

It always appeared to me remarkable, in considering this result, that trimethylenedicarboxylic acid if it really were a trimethylene-derivative should not combine with bromine at all. In order to test this, I dissolved some of the acid in chloroform, added an excess of bromine, and let the mixture stand 14 days in the dark. At the end of this time, no apparent change had taken place, and on allowing the mixture to evaporate in an open dish a white crystalline acid was obtained, which proved to be unaltered trimethylenedicarboxylic acid. The same results were also obtained by Roeder (*Annalen*, **227**, 18), and Fittig, in his theoretical paper on the constitution of vinaconic acid (*ibid.*, **227**, 29), comes to the conclusion that this acid is either not at all, or at all events only very slightly, acted on by bromine at ordinary temperatures.

Fittig and Marburg at a later date (*Ber.*, **18**, 3413) repeated the experiment in sunlight, and found that under those conditions a change did slowly take place, a brominated acid of the formula $C_3H_4Br_2(COOH)_2$ being formed, a result which shows now clearly the perfect analogy existing between the reactions of trimethylene itself and those of its dicarboxylic acid.

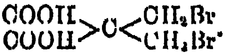
The further examination of this dibromo-acid must prove conclusively whether trimethylenedicarboxylic acid really is a trimethylene-derivative or not. If this is so, the dibromo-acid must have one of the two following formulæ:—

I.



$$\begin{matrix}COOH\\COOH\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CH_2Br\\Br\end{matrix}.$$

II.



$$\begin{matrix}COOH\\COOH\end{matrix}{>}C{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix}.$$

Whereas if it be vinylmalonic acid, the dibromo-acid must have the formula—

$$(COOH)_2{\cdot}CH{\cdot}CHBr{\cdot}CH_2Br.$$

Some very interesting experiments, which tend strongly to support the trimethylene formula for the acid in question, have lately been instituted by Franchimont (*Rec. Trav. Chim.*, 1885, 398 and 399). This chemist has, during the course of his experiments on the action of pure nitric acid on organic compounds in the fatty series, made the discovery that mono-substituted malonic acids when treated with pure nitric acid are completely and rapidly decomposed with evolution of 2 mols. of carbonic anhydride, whereas the di-substituted malonic acids under similar treatment remain perfectly unaltered.

Franchimont was kind enough to include trimethylene- and tetramethylene-dicarboxylic acid in his investigation, and as a result he found that these two acids behaved exactly as di-substituted malonic acids. Even after standing for 10 days with the nitric acid, not a single bubble of carbonic anhydride was evolved in either case, and on extracting with ether he was able to recover almost the entire quantity of the acids unchanged.

Turning from the chemical to the physical properties of trimethylenedicarboxylic acid, it is interesting to see that here also all the experiments which have been made on the refractive index and magnetic rotation of the ethylic salt of this acid fully bear out the view that it is really a trimethylene-derivative and not vinylmalonic acid.

Dr. Gladstone was kind enough to determine the refractive index of ethylic trimethylenedicarboxylate, and has given me the following account of his experiments; the measurements were made at a temperature of 7°:—

Specific gravity .... = 1·0708
Refraction for A............ = 1·4351
„ D............ = 1·4399
„ H............ = 1·4554
Specific refraction for A .... = 0·4063
„ dispersion „ „ .... = 0·0190
Refractive equivalent A .... = 75·57

The conclusion which Dr. Gladstone draws from these experiments is that ethylic trimethylenedicarboxylate is a saturated compound. The calculated refractive equivalent of a substance of the formula $C_9H_{14}O_4$ is 75·6, a number which agrees closely with that found.

Again, the dispersion of a saturated substance of this formula should be about 0·0190, which was actually found. If, on the other hand, this ethereal salt had contained a double band, the dispersion would have been from 0·0240 to 0·0250.

The experiments on the magnetic rotation of ethylic trimethylenedicarboxylate, which were conducted by my father, show also very clearly that this substance must be a saturated body. The following are the results of his experiments:—

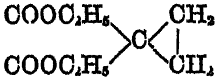
Specific gravity:

$$d\frac{15^\circ}{15^\circ} = 1{\cdot}06455,$$

$$d\frac{25^\circ}{25^\circ} = 1{\cdot}05657.$$

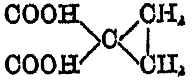
t.	Sp. rotation.	Mol. rotation.
17·0°	0·9154	9·191
17·5	0·9139	9·180
18·0	0·9136	9·181
18·5	0·9389	9 138
14·4	0·9116	9·136
14·4	0·9113	9·162
14·4	0·9165	9·183
14·8	0 9135	9·157
Average 16·1	0·9134	9·166

The calculated molecular rotation of a saturated substance of the formula—

,

would be 8·842, whereas the calculated magnetic rotation of ethylic vinylmalonate is 10 258. The numbers found show, therefore, clearly that the substance is not ethylic vinylmalonate.

From the results of all these experiments, it is extremely probable that trimethylenedicarboxylic acid (1, 1) really has the formula—

.

I hope at some later date to be able to prepare vinylmalonic acid, in order that it may be possible by direct comparison to decide between these two formulæ.

LXXXVI.—*Experiments for the purpose of Comparing the Equivalent of Zinc with that of Hydrogen.*

By Lieutenant-Colonel H. O. Reynolds, late R.E., and Professor W. Ramsay, Ph.D.

CONTENTS.

		PAGE
1.	Object of Investigation	854
2.	Explanation of Apparatus and Diagram	855
3.	Calibration of Apparatus	856
4.	Purification of Metal	857
5.	Weight of Metal how obtained	857
6.	Barometer	859
7.	Thermometers	859
8.	Expansion of Apparatus	859
9.	Exhaustion of Air from Apparatus	860
10.	Description of an Experiment	860
11.	Process of taking Readings	862
12.	Calculation of Results	863
13.	Statement of Results	864
14.	Diagram	864

The object of the present investigation, as originally proposed, was to make a direct comparison between the atomic weight of the element hydrogen and the atomic weights of several of the metallic elements.

It is manifest that in such a comparison the sources of error are smaller than in most of the methods used in atomic weight determinations, and also, as is pointed out by Clarke in his "Constants of Nature," the results cannot be influenced by errors in the atomic weights of other elements. So many difficulties, however, presented themselves before a correct method of working was realised, that only one element—zinc—has as yet been compared. It is intended at some future time to compare several other elements in the same way, and also to use the process about to be described in the comparison of the equivalent of oxygen with that of hydrogen. The comparison of these two elements is, of course, the basis of the whole of the atomic weight determinations, and as Ostwald (*Lehrbuch*, 1, 41—44) shows, it is most important that the exact relative weights of these two gases should be redetermined. Clarke in discussing the results already obtained for zinc shows that Erdmann's work is the most reliable, and this is the only one of the earlier results that need here be noticed.

As Ostwald (*Lehrbuch*, 1, 113) gives the earlier results and the references to the original papers, the details are not given here.

The following are the results obtained by various experimenters in each case given after reduction to the two recognised standards:—

	Date.	Name.	O = 16.	O = 15·9633 H = 1·0000
1.	1843.	Erdmann............	65·07*	64·9045
2.	„	„	65·04*	—
3.	1883.	Marignac............	65·330*	65·180
4.	„	„	65·290*	65·140
5.	1883.	Baubigny............	65·334^{S}	65·184
6.	1884.	Van der Plaats	65·330	65·180^{H}
7.	Ostwald accepts		65·380*	65·230
8.	Clark accepts		65·053	65·9045*
9.	Determination now made		—	65·4787^{H}

Most of these values depend on oxygen. A * is attached to those numbers where this is the case. For Baubigny's result O = 16, but two values are given depending on whether sulphur = 32·074 or 32·00.

The work of Van der Plaats might be compared with the present results, as it was a direct comparison with hydrogen, but his figures are given without any description of the process by which they were obtained. His result 65·18 corresponds well with that now obtained in the preliminary experiments, namely, 65·2430. It is usual to accept the values obtained by Regnault for the specific gravities of hydrogen and oxygen, and this has been done in the present instance.

The idea that has been now worked out is that an accurately known weight of metal, purified with the greatest care, is to be dissolved in an acid in an apparatus so contrived that all the hydrogen liberated can be collected, its volume very accurately measured, and hence its weight found.

By the comparison then of the weight of the metal with the weight of the hydrogen the exact equivalent of the metal can be obtained, and, assuming the valency of the metal, its atomic weight follows.

Explanation of Apparatus and Diagram.

The general arrangement of the apparatus for evolving, collecting, and measuring the hydrogen is shown by the diagram (p. 864). The air-pumps and gauges are not shown.

A is a glass globe of about 1200 c.c. capacity. Its stem B has a millimetre scale cut on it, by means of which the volume of the gas in A and B down to any point can be read. The length of B is about 400 mm., of which 350 mm. are divided.

The stem B is connected with the bent tube FGH, into which water can be admitted from the bulb E, so that not only can the gas in A and B be confined by the water, but by altering the position of E vertically a varying head of water can be brought to bear on the gas in AB.

Bulb D contains the dilute acid which is to be admitted into bulb C.

Bulb C contains the metal, and in it the hydrogen is evolved on the admission of the acid from D.

The gas as it is liberated rises from C into B and A.

A glass cylinder K surrounds A.

The jackets of glass tubing L and N surround tube B and part of tube GH. The vessel K and jackets L, N are all connected, so that water can flow freely from one into the other.

The water enters from the tap O, fills K, runs through L, thence by tube M into N and out by P.

This flow of water enables the apparatus to be kept at a fairly constant temperature when required.

The glass bulb Q is to contain any small accidental excess of water in the tube FG.

T is a thermometer suspended in the water in K.

T_1 is a similar thermometer suspended inside the jacket N.

S is a glass mirror, the face of which is engraved with a scale of millimetres, and enables the levels of the water in tubes BF and GH to be read.

The apparatus is constructed chiefly of glass.

The junctions are made with thick rubber tubing and rubber corks, which are all wired and paraffined, and on trial were found not to leak.

The rubber tubing connecting D with C, and E with GH, has $\frac{1}{8}$-inch bore and thick sides. The small tubes leading to the Sprengel and air-pump are of lead of $\frac{1}{8}$-inch bore.

Calibration of the Apparatus.

In order to ascertain the content of the globe A and its stem B, and also the value in c.c. of the millimetre divisions engraved on B, the globes A and B were weighed first when dry, and again twice when filled with water up to two different division marks on the stem, the temperature being taken at the same time. The capacity in c.c. at 0° C. was thence calculated.

The tables given in *Watts' Dictionary* for the expansion of water were used. A similar process gave also the approximate content of AB down to the point marked * (see diagram), together with the content of C and its tubes leading into B.

This was used in calculating the volume of the air left in the apparatus after exhausting most of the air.

These measurements for calibration were all made twice.

Purification of the Zinc.

The zinc worked with was at starting that sold as free from arsenic and other common impurities. This was dissolved in dilute sulphuric acid free from lead. The zinc sulphate was crystallised several times, and finally the solution of the sulphate in water was electrolysed. It was supposed that the metal thus deposited on a platinum wire electrode would be pure. It was, however, found that its composition was not even constant, and that some unknown impurity, probably arsenic and zinc oxide, existed in it. Samples of the zinc thus prepared were used in the first 21 experiments, and gave very varying results.

In order to prepare another sample free from impurity, about 45 grams of this electrolytically deposited zinc, which was certainly purer than any other procurable, was first dissolved in dilute hydrochloric acid, the zinc was then precipitated as hydrate with ammonia, and the precipitate redissolved in excess of ammonia. A precipitate of zinc sulphide free from other metals was thrown down by hydrogen sulphide. The zinc sulphide thus obtained had a slight reddish-brown tinge in the layer first deposited. The upper layer was pure white, and was separated from the coloured portion which was not used.

This zinc sulphide was again put through the above process, and then the pure sulphide after being well washed was dissolved in pure dilute sulphuric acid and crystallised several times. A solution of this sulphate in water was then electrolysed.

The zinc as thrown down on a platinum wire electrode was difficult to dry, as it was deposited in branching crystals. It was, therefore, melted in a hard glass tube exhausted of air, and when fluid was run so as to form a thin bar of clean metal which could easily be broken up for weighing.

For two experiments (both of which failed from the excessive difficulty of getting the acid to act on the very pure metal) a portion of this metal was volatilised in an exhausted tube of hard glass. The sublimed metal appeared to be so pure that it was nearly unacted on by sulphuric or hydrochloric acid.

Weight of Zinc—how Obtained.

The weights used were made by Westphal, and were of the ordinary pattern and arrangement. Above 0·1 gram, they were of brass platinised; their density was found = 8·41. The smaller weights were platinum foil; their density was assumed = 21·5. The riders were aluminium.

The 50-gram weight was (through the kindness of Mr. Chaney) first standardised in the Standards Office in London by being compared with a 50-gram weight of known value. The other weights above 0·1 gram were then weighed against this 50-gram weight, and their values both in air and in a vacuum obtained by the usual process. The platinum weights and the riders were assumed to be nominally correct in air.

The balance was carefully adjusted and the difference of the lengths of the arms and the weights of the pans ascertained and neutralised as far as possible. The method of weighing adopted was that used in the Standards Office in comparing weights. The balance error was thus eliminated. In each experiment, the value of a milligram weight was found in terms of the divisions of the balance scale. The following calculation then gave the true weight of the metal:—

(1.) The values of the weights above 0·1 gram were already known.

$$\text{The value of the platinum weight} = \frac{\left\{\begin{array}{c}\text{nominal value}\\ \text{in air in}\\ \text{mgrms.}\ \ldots\end{array}\right\} \times \overset{\substack{\text{Value of 1 Pt gram}\\ \text{in a vacuum.}}}{999\cdot94338}}{1000}$$

Then

$$\left.\begin{array}{l}\text{Sum of all the weights used in air.}\\ \textit{Less}\ \text{do. do. do. in a}\\ \quad\text{vacuum}\ldots\ldots\ldots\ldots\end{array}\right\} = \left\{\begin{array}{l}\text{Weight of the air dis-}\\ \text{placed by the weights}\\ \text{used.}\end{array}\right.$$

$$\text{(2.)}\ \left.\begin{array}{l}\text{Nominal value in air of all}\\ \text{the weights used in grams..}\end{array}\right\} \times \left\{\begin{array}{l}\text{Weight of air displaced by}\\ \text{a kilogram weight of the}\\ \text{same density as the metal}\\ \text{being weighed.}\end{array}\right.$$

$$= \text{Weight of air displaced by the metal being weighed.}$$

(*Note.*) A kilogram weight of density (same as assumed for zinc) = 7·12 displaces 170·84 mgrms. of air.

(3.) Then

$$\left.\begin{array}{l}\text{Weight of air displaced by metal..}\\ \textit{Less}\ \text{weight of air displaced by}\\ \quad\text{weights}\ldots\ldots\ldots\ldots\end{array}\right\} = \left\{\begin{array}{l}\text{Excess weight of air dis-}\\ \text{placed by metal being}\\ \text{weighed.}\end{array}\right.$$

$$\text{(4.)}\ \left.\begin{array}{l}\text{The value of the weights used}\\ \quad\text{in a vacuum}\ldots\ldots\ldots\\ \quad\textit{Less}\ \text{excess weight of air dis-}\\ \quad\text{placed by metal}\ldots\ldots\end{array}\right\} = \left\{\begin{array}{l}\text{True value of weight of}\\ \text{metal in a vacuum.}\end{array}\right.$$

(*Note.*) If the density of the metal being weighed is greater than that of the weights used, then, in (4), the word "less" will become "plus."

It was ascertained that the errors caused by neglecting the corrections for latitude and height above sea-level, also for temperature and moisture in the air, were so small as to be well within the unavoidable limits of error occurring in other parts of the operations. These corrections were therefore omitted.

Barometer.

The barometer used was of the usual open syphon pattern, the portion of the tube where the reading was taken was made of a large bore (and of thin glass) so as to eliminate almost wholly the error due to capillarity. The mercury was boiled in the barometer-tube above the air-trap after being filled.

Several instruments were tried until one was found practically free from error. A glass jacket was placed round the longer limb of the barometer-tube to allow of a continuous current of water from a tap being run through it during the whole time that readings were being taken. This was to prevent any alteration of the temperature of the room affecting the height of the mercury.

A glass mirror having a millimetre scale engraved on it was used for reading the levels of the mercury.

To afford a check on the readings, two were in each case taken quickly, one after the other, on different parts of the scale. There was an arrangement by which the barometer-tube could be shifted up and down in front of the scale for the above purpose.

The two readings were not accepted until the difference between them was within 0·1 mm.

Thermometers.

Three thermometers were used at once when taking readings. They were all made by Negretti and Zambra, and read to 0·1° C. One was hung inside the jacket of the barometer, one (T) suspended in the water in vessel K (see diagram), and the third was hung inside the jacket to the tube H.

All three instruments were tested both against a standard and also by finding the error of their zero points when placed in melting ice.

Expansion of Apparatus.

The content of the apparatus having been ascertained at 0°, the content at the temperature of any reading was calculated and a correction made to the apparent volume of the gas for each reading.

The coefficient of the cubical expansion of glass was taken as 0·0000255 per 1° C.

Exhaustion of Air.

Two pumps were used in exhausting the air from the apparatus. The larger portion of the air was quickly extracted by a Carré pump, and then a five-fall Sprengel removed the remainder; a very high vacuum was never needed. In the globe A, about 2 mm. of mercury was the highest vacuum used.

It was eventually found best to exhaust the air whilst keeping the apparatus at as nearly as possible the same temperature as that at which the readings would subsequently be taken. This was done by keeping the tap water flowing. Heating the apparatus with hot water whilst it was being exhausted gave a higher vacuum, but then it was not certain that part of the hydrogen would not be lost subsequently, owing to its supplying the place of the air driven off from the glass by the heat.

In the first few experiments the apparatus was filled with distilled water and the hydrogen was made to displace it. It was found, however, that some of the hydrogen was absorbed by the water, and apparently the percentage was not quite constant. Thus the subsequent experiments came to be made after exhausting the air.

Description of an Experiment.

The following is as concise a description of one experiment as can be given. It would be impossible to mention every detail.

Bulb D having been three-fourths filled with the dilute acid (about one of acid to three of distilled water) and bulb E with distilled water, were well corked with rubber corks. Through each cork two glass tubes passed, one short to connect with the rubber tubing, the other long enough to reach the bottom of the bulb. The latter was drawn to a point and sealed at its outer extremity.

Both bulbs were then boiled over a water-bath, being at the same time exhausted of air. When the air had all been boiled off, the clips on the rubber tubes were closed and the bulbs inverted.

The barometer was then read approximately and a rough calculation made for the weight of metal to be used by assuming such a temperature and pressure that the gas to be evolved should, at atmospheric pressure, fill the globe A and reach half way down the stem B. The metal was then weighed as before described to obtain the exact weight. The metal after weighing was placed in a small glass tube having a short stem of glass rod. Some pieces of platinum foil were placed along with the metal. This tube was then inserted from below into the empty bulb C, which was then tightly corked and thus connected with bulb D by means of the long rubber tube (see diagram).

The large globe A with its stem B and the tubing F, G, H, and the small bulb Q, were then connected with the air-pumps by the leaden tube above H.

The water was set running through the jackets and the air-pumps kept working until the gauge showed a sufficient vacuum. The clip to bulb Q was then closed.

The clip to bulb E was then slightly opened until sufficient water had run in from E to fill the tubing H, G, F, B up to about the levels marked *.

The water-levels in H, G, F, B having been allowed to adjust themselves, and the water in the jackets being still kept running, and the Sprengel pump working, the exact levels of the water in each limb of the tube H, G, F, B was read on the scale S, and at the same time the thermometers T, T_1 were read. From these readings and from the previously-ascertained content of the apparatus, the pressure of the air still remaining in it was obtained for use in the subsequent calculations. The clip above H was then closed, thus shutting off the air-pump. The metal, the exact weight of which was known, was thus enclosed in a vessel exhausted of air and capable of containing all the hydrogen that might be liberated in bulb C, the water in B, F, G, H acting as a stopper to prevent the gas escaping from A, B.

The sealed points of the tubes in D and E were then broken. This admitted the air above the liquid in the bulbs, and provided a pressure to be utilised in forcing the liquids from D and E into the apparatus against the back pressure from the hydrogen. Air was thus prevented from mixing with the liquids in the bulbs D, E, and as the rate of diffusion of air in a liquid is very slow, practically no air was ever carried by the liquids into the apparatus. The clips to D and E were then simultaneously opened. The acid from D was admitted into C as quickly as possible so as to fill about three-quarters of C. The acid acted instantly on the metal in C and hydrogen was rapidly liberated.

The clip to bulb E was opened more gradually to admit the water into the tubes H, G, F, B, so as just to compensate for the gradually increasing pressure of the hydrogen escaping from C into B, A. The level of the water in BF was thus kept at the point marked *, the water in GH at the same time slowly rising until at length the tube GH was completely filled with water.

After that, the apparatus was left to itself until all the metal in C was dissolved and all the hydrogen had been given off.

The clip to bulb D was then opened and liquid allowed to run into C so as to fill it and its connecting tubes, and thus force all the hydrogen up into A, B. Care was taken not to allow the acid from C to flow over into B, as the vapour-pressure of the water in A, B might thereby have been altered.

The top clip above C was then closed, the clip to E opened, and the water flowing into GFB forced up the hydrogen in FB and confined it in A, B above all the junctions or any possible means of escape. The time taken to dissolve the zinc varied from two hours to two days. In some cases hydrochloric acid, in others sulphuric acid was used.

A small portion of the hydrogen became absorbed by the liquid in bulb C. In order to collect this, C was connected to the pumps by the leaden tube as shown at the side of C. C was then surrounded by a water-bath and boiled, and the air from the connecting tubes having been exhausted, the side clip to C was opened. All the absorbed hydrogen was thus drawn off from C, and collected by the Sprengel in a small graduated tube. The volume of this gas was measured, and after reduction was added to the gas found in AB.

The small portion of the liquid which boiled over from C during the above process was caught in a separate bulb, kept cooled. About 4 c.c. of hydrogen was usually collected in this way from 350 c.c. of liquid in C. This gives about 1¼ per cent. absorption of hydrogen in the dilute acid and solution of zinc salt.

Process of taking the Readings for Volume.

When about to take the readings for finding the volume of the gas in A, B, communication was first made with the atmospheric pressure above the clip at H. The clip at H was then slowly opened. The water in HG fell in the tube and pushed up the water in FB, thus driving up the gas in BA until equilibrium was established. The tap water was then set quickly running in the jackets and vessel K. Bulb E was so arranged that it could be slid up and down and fixed at any desired height. Bulb E was then so adjusted that the water and gas level in B was as low down as possible within the limits of the scale on B. The water-level in GH at the same time adjusted itself usually about the level of N. The apparatus was then left standing for about an hour (the water all the time running through the jackets). This was to allow time for the gas and apparatus to take up a steady temperature and for the pressure to adjust itself.

The barometer was next carefully read as before described. Thermometers T, T_1 were then read as quickly as possible. The water-level in B was read at once for volume, on the scale cut on B. The water-levels in B and GH were also at once read for head of water on the scale S. The thermometers T, T_1 were again quickly read. This completed one reading. Usually seven readings were thus taken in each experiment.

The temperature was found to remain practically constant during the time of taking a set of seven readings, owing to the running water. Both thermometers agreed closely in their readings. The above process was repeated for each reading.

The barometer was read approximately between each reading to prevent any serious and sudden change of pressure being overlooked. At the end of a set of readings the barometer was again read as carefully as at the commencement. A correction could then be applied to each reading for any slight change that might have occurred. It was found to give better results if the readings were commenced from the lower end of the tube B. The first reading taken at the lowest possible level, after waiting the hour, always gave a high value. This lowest reading ought always to be discarded. It appeared as if the vapour-pressure did not adjust itself at this lowest point within the hour of waiting, but that the slight compression of the gas from being forced up for the next and following readings enabled the vapour-pressure to adjust itself to its normal condition at once.

The water-levels were extremely sensitive to the slightest external alteration of pressure from any cause, such as a sudden gust of wind, the slamming of a door, &c.

From the above process, the data obtained were, barometer reading, temperature, apparent volume of hydrogen, head of water. Previously the known values were weight of metal, pressure of air in the apparatus after exhaustion, the volume of hydrogen absorbed in bulb C. From these conditions, the calculations for the atomic weight could be made.

Calculation of Results.

The calculations were made in the ordinary manner. All the readings for volume and pressure were reduced to normal conditions. The assumptions made were—

Valency of zinc = 2.

Weight of a litre of hydrogen = 0·0896 gram.

Specific gravity of mercury = 13·596.

Absolute temperature = thermometer reading + 273.

A gas expands $\frac{1}{273}$ of its volume for each 1° C. of absolute temperature.

The vapour-pressure of water was taken from Regnault's tables.

The usual correction for temperature was made to the barometer readings.

The general formula used may be thus written:—

Atomic weight = equivalent × valency—

$$= \frac{2 \times \text{weight of zinc} \times \text{absolute temperature} \times 760}{\text{vol. of gas} \times 0{\cdot}0896 \times 273 \times \text{pressure}}$$

(*a*.) The volume of the gas was corrected for expansion of apparatus, and then the true volume of the gas extracted from C was added.

(*b*.) The "pressure" was found by correcting the barometer reading thus:—

— Temperature correction for alteration of volume of the mercury and expansion of glass scale.

— Vapour-pressure of water at temperature of reading.

— Pressure of residual air after exhausting, reduced to 0° C.

± Head of water at time of reading reduced to its equivalent in mercury.

This calculation was worked out for each reading, and the mean taken as the result of the experiment.

Statement of Results.

Altogether, 29 experiments were made. Out of this number, four had to be rejected entirely.

The nine first were not fully corrected, as it was only afterwards that all the corrections necessary were understood. These nine were therefore rejected. The next 11 were considered only as preliminary, as though all corrections were applied yet some of them were means from subsequent experiments. The next five experiments were carried out without any known source of error, and these results are fairly concordant.

The mean result of the 11 preliminary experiments is 65·2430.

The five results considered correct are—

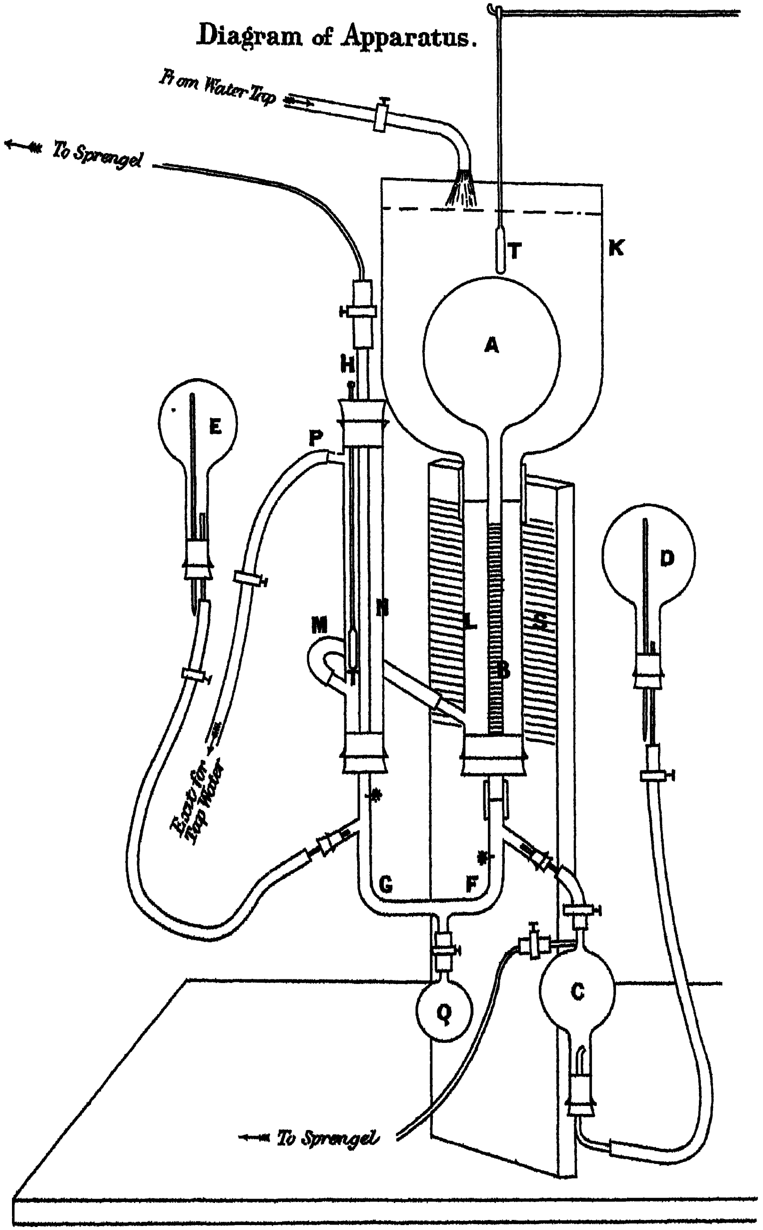
	65·5060
	65·4766
	65·4450
	65·5522
	65·4141
Mean....	65·4787 ± 0·016135

The details from which these five values were calculated are given in the following tabular statement:—

RAMSAY & REYNOLDS.

Journ Chem Soc Dec 1887

Diagram of Apparatus.



Harrison & Sons Lith. St Martins Lane W C

■

No. of reading.		Weight in a vacuum of metal zinc.	Reduced volume of hydrogen.	Reduced pressure.	Thermometer reading, mean 0° C.	Results.
		grams.	c.c.	mm.		
1	1	3·2995842	1216·86	729·18	10·54	65·5195
	2		1219·64	727·78	10·54	·4960
	3		1222·73	725·78	10·54	·5105
	4		1225·62	724 08	10·54	·5094
	5		1233·05	719·72	10·53	·5068
	6		1230·54	721·10	10·48	·5033
	7		1228·02	722·65	10·48	·4969
					Mean...	65·5060
2	1	3·3664971	1201·62	754·52	10·72	65·4641
	2		1205·15	752·25	10·74	·4739
	3		1206·88	751·14	10·73	·4744
	4		1209·76	749·37	10·73	·4729
	5		1212·09	747·84	10·73	·4789
	6		1213·40	747·02	10·73	·4817
	7		1217·02	744·70	10·73	·1903
					Mean...	65·4766
3	1	3·3001116	1203·09	735·56	9·48	65·4595
	2		1206·16	733·75	9·46	·4476
	3		1218·85	726·03	9·47	·4584
	4		1216·02	727·89	9·47	·4436
	5		1212·74	729·97	9·47	·4335
	6		1216·16	731·42	9·46	·4108
	7		1207·72	733·00	9·46	·4317
					Mean...	65·4450
4	1	3·4111156	1218·56	747·90	6·42	65·5599
	2		1216·43	749·38	6·42	·5450
	3		1214·59	750·58	6·42	·5394
	4		1212·73	751·71	6·42	·5412
	5		1200·68	753·30	6·41	·5630
	6		1205·70	755·85	6·80	·5552
	7		1202·12	758·27	6·42	·5421
	8		1200·21	755·36	6·40	·5724
					Mean...	65·5522
5	1	3·3754049	1222·25	738·31	8·51	65·4825
	2		1220·07	789·96	8·57	·4172
	3		1216·31	742·26	8·57	·4161
	4		1213·71	743·87	8·56	·4120
	5		1210·92	745·67	8·58	·4091
	6		1208·57	747·12	8·56	·4045
	7		1206·15	748·54	8·55	·4090
	8		1203·73	749·94	8·53	·4127
					Mean...	65·4141

It seems possible, therefore, that the true atomic weight of zinc is 65 50.

The readings in each set of the last two experiments worked out so far concordantly that they show the apparatus is well adapted for the accurate measurement of the volume of a gas.

If, therefore, the metal can be thoroughly purified and accurately weighed, the process described affords a very accurate means of determining the atomic weight of several of the elements.

University College, Bristol,
May, 1887.

LXXXVII.—*Note on the Atomic Weight of Gold.*

By T. E. Thorpe, F.R.S., and A. P. Laurie, Esq., B.A.

In a communication which we had the honour of laying before the Society last session, and which is published in the Transactions, 1887, p. 565, we gave the results of a series of estimations of the atomic weight of gold, based on the determination of the relation between gold and potassium bromide, gold and silver, and gold and silver bromide. The method employed by us consisted in heating potassium bromo-aurate to a temperature sufficiently high to convert the salt into a mixture of gold and potassium bromide, and then determining the proportion of gold to potassium bromide in the decomposed salt. Eight determinations made in this way gave the final value Au = 196·876 (H = 1). The amount of silver required to convert the potassium bromide of the decomposed salt into silver bromide was then ascertained, and a second value for Au obtained from the relation of Au to Ag. Nine experiments gave, as a final value, Au = 196·837. The silver bromide formed was next weighed, and a third value for Au obtained by comparing the weights of Ag, Br, and Au. Eight experiments made in this manner gave Au = 196·842. The mean of the three series is 196·852, which number we accordingly adopted as the most probable value for the atomic weight of gold.

Whilst our observations were in progress, Hr. Gerhard Krüss published a paper on the same subject in the *Berichte* for February, 1887. Krüss also employed potassium bromo-aurate, but, as we pointed out in our paper, the validity of his method of treating the salt depended upon the assumption that it could be made absolutely anhydrous by heating without losing bromine, and that it was so slightly hygroscopic that it could be weighed without risk of absorbing moisture. We had convinced ourselves that neither of those conditions could be secured, and we had, therefore, so arranged our plan of work as to obviate the necessity of either drying the bromo-aurate, or of knowing its weight. We also pointed out in discussing Herr Krüss' experiments that his results were necessarily affected by these circumstances, and hence that his final value Au = 196·64 was probably too low.

In a paper recently published in the *Berichte*, 20, 2365, Herr Krüss admits the presence of uncombined gold in his bromo-aurate, but states that free gold invariably occurs in the double salt, and that it cannot be removed even by repeated crystallisation. According to Herr Krüss, the amount of the free metal would appear to be perfectly constant, since after three or four or even eight recrystallisations the total amount of gold, that is free and combined, contained in the double salt was invariably the same. Nevertheless, on treating the double salt with water, minute quantities of uncombined gold remained undissolved.

There is no doubt whatever that under certain circumstances free gold may be readily obtained on dissolving the bromo-aurate in water. The solution has only to remain exposed to the air for a short time when, simply by the falling into it of atmospheric dust, minute quantities of gold will gradually make their appearance on the surface of the liquid, and in the form of the "Flitterchen," which Herr Krüss describes. Organic matter present in the distilled water will act in a similar manner. Filtration through paper is immediately attended with the separation of small quantities of the metal. The action of organic matter upon solutions of gold is, however, so generally known that, we should imagine, it would be hardly lost sight of in a research of this character.

Now, because Herr Krüss was not able to prepare a pure sample of the double salt, he makes the assumption that we also were equally unable to do so. Our potassium bromo-aurate must, he says, have necessarily contained free gold, and to the extent of 0·0499 per cent. This particular number he obtains by dissolving a quantity of one of his own preparations in water, and weighing the amount of undissolved gold. He assumes that the amount of the reduced gold is the same in all samples of the bromo-aurate, no matter how different might have been the conditions of their preparation. He then proceeds to apply this amount as a correction to our results, whereby they are brought into very fair accord with his own. It ought, however, to be stated that Herr Krüss had previously treated his own observations in the same way, and had thus brought the results of his analysis of the bromo-aurate into a closer accordance with the numbers he had obtained by the analyses of the neutral chloride, and which were apparently unaffected by any possible reducing action of organic matter.

As a matter of fact, there is no very great difficulty in preparing the double bromide free from any sensible quantity of uncombined gold, provided that proper and obvious precautions are taken. We believe that we took such precautions. We can at least affirm that we frequently dissolved quantities of from 8 to 19 grams of our preparations in water without the slightest trace of free gold being seen. Even had we been ignorant of the possible reducing action of atmospheric dust, the manner of our work would tend to minimise its effect. We cannot pretend, of course, that dust was wholly excluded. But it is quite certain that in none of our preparations was there an amount of free gold sufficient to account for the difference of 0·21 between our own and Krüss's final values. So far as the present evidence goes, therefore, we altogether dissent from Herr Krüss's conclusion that the lower value 196·64 is to be preferred as the more correct expression for the atomic weight of gold.

Indeed, there is some reason to believe that even our own number may turn out to be slightly below the truth. At the last meeting of the British Association, Professor Mallet, of the University of Virginia, communicated a preliminary account of a research which he has in progress on this question. Complete details of his methods have not yet been published, but he announces that the results already obtained indicate that the atomic weight of gold is certainly not lower than 196·8.

LXXXVIII.—*Certain Products from Teak.* Preliminary Notice.

By R. Romanis, D.Sc., F.C.S., Rangoon College.

It is commonly stated in works on Indian forestry that teak yields an oil by distillation which is used as a varnish. Last year a specimen of this varnish was required for a collection of forest products, but it was found that the natives of the country know nothing of it, and there can be little doubt that the statement referred to originated in a confusion between the teak tree and the kanyin, a species of Dipterocarpus which yields gurjun oil and a fine timber.

I was desired to ascertain if the oil could not be extracted in any other way. On examination, I found that alcohol extracts about

6 per cent. of a soft resin from teak but no oil or varnish. This resin is a mixture of several substances. When extracted from freshly cut teak, it is entirely soluble in chloroform, but the resin from wood that has been long exposed to the air is only partly soluble; this change is due to oxidation. A specimen of the resin which had been long exposed to the air gave the following results on combustion:—

C............	60·91
H............	6·81
O............	32·28

Whilst the substance insoluble in chloroform gave—

C............	60·20
H............	6·98
O............	32·82

The substance soluble in chloroform gave results which varied with the time it had been prepared and the temperature at which it was dried.

	I.	II.	III.
C	75·20	74·91	73·48
H	9·25	7·17	9·38
O	15·55	17·92	17·14

It was found that the resin melts below 100°, and gives off volatile products, principally a substance that sublimes in dendritic forms and crystallises from alcohol in spirals or in stellate groups of prismatic crystals. It is also found as an efflorescence in soft feathery crystals on the surface of the resin when this is kept for a few months.

When the resin is distilled, the distillate is a felted mass of crystals having a sweet smell like that of myrrh or incense, whilst a black shining coke is left in the retort; the crystalline substance may be purified from adhering oil by recrystallisation from hot alcohol, but it seems to retain the last traces with great obstinacy. When teak is exposed to destructive distillation the following products are obtained:—

Heavy tar..............	10·6	p.c.
Watery distillate........	36·0	„
Light oil	3·4	„
Charcoal...............	35·0	„
Uncondensed...........	15·0	„
	100·0	

The tar contains the crystalline substance in considerable quantity; it may be extracted by adding an excess of caustic soda, when much heat is evolved and the substance is precipitated as a curdy mass which soon becomes crystalline. It is purified from the soda solution by washing and crystallisation from hot alcohol. The analysis points to the formula C_9H_8O as the lowest possible. Burnt with oxide of copper in a stream of oxygen it gave the following results. I give the whole series:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	81·18	81·58	81·52	81·67	80·20	81·22	80·47	80·82
H	9·70	7·33	7·28	6·05	6·47	6·28	6·12	6·54

The first three must obviously be rejected, as the oxide of copper had not got into working order. No. IV was I believe the purest preparation. The hydrogen is naturally high, as the work was performed in an atmosphere saturated with moisture at 30° C. C_9H_8O requires C 81·8, H 6·06. This substance is partially decomposed on heating, hence its vapour-density could not be determined by V. Meyer's method, which gave results ranging from 86 to 50. Among the products of decomposition was an oil with the odour of beeswax.

The crystals dissolve in sulphuric acid with a yellow colour, and are precipitated on dilution. Nitric acid acts in a similar way, but on heating it with a mixture of the two acids, and diluting with water, a yellow nitro-derivative was precipitated. On washing the precipitate with hot alcohol, a crimson substance with a golden surface colour was extracted.

The yellow nitro-derivative dissolves when heated with strong sulphuric acid, forming a red solution from which water precipitates purple flocks, soluble in alkali with a bright blue colour.

The yellow compound gave on analysis—

	I.	II.	III.
C	57·71	57·69	58·27
H	4·70	4·0	4·12

The crimson substance—

C................	57·35
H................	5·13

The purple substance—

C................	42·0
H................	4·56

I had only very small quantities at my disposal and I have not been able to repeat the analysis. On making a second preparation of the nitro-derivative the action was stopped after half an hour instead of allowing it to go on one and half hours; in this case, as at first, a product was obtained which gave 65 40 per cent. C and 5 91 H.

From these reactions it may be inferred that the new compound is a quinone, $C_{18}H_{16}O_2$, and that the products obtained by the action of nitric acid were in the first case a dinitro- and in the second a mixture in equal parts of the di- and mono-nitroquinone, and the coloured products are analogous to those obtained from anthraquinone under similar conditions. When treated with sodium amalgam in alcoholic solution, the liquid in contact with the amalgam first turns crimson, but as it mixes with the solution it becomes green and then yellow, and the original substance is reproduced. Sodium amalgam acting on the crystals under the surface of ether turns them into a green mass, which on exposure to the air rapidly decomposes into caustic soda and the original compound.

The quinol corresponding with this compound, which may be named *tectone*, is therefore very unstable. There are other coloured derivatives which have not yet been examined, but I have set up apparatus for the destructive distillation of teak on a larger scale, and hope soon to be able to communicate the results to the Society.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1887.

A.

Apjohn, J., obituary notice of, 469.

Armstrong, H. E., an explanation of the laws which govern substitution in the case of the benzenoid compounds, 258, 583.

—— note on the influence of liquid water in promoting the interaction of hydrogen chloride and water on exposure to light, 806.

B.

Bailey, G. H., the determination of atomic weights by means of the normal sulphate, 676.

Bailey, G. H., and G. J. **Fowler**, suboxide of silver, Ag_4O, 416.

Baker, C. J., absorption of gases by carbon, 249.

Barff, F. C., obituary notice of, 471.

Brown, A. J., further notes on the chemical action of *Bacterium aceti*, 638.

Burton, C. L. See F. R. **Japp**.

Butlerow, A. M., obituary notice of, 472.

C.

Carnegie, D. J. See M. M. P. **Muir**.

Carnelley, T., and A. **Thomson**, derivatives of tolylbenzene, 87.

Cleminshaw, E. See F. R. **Japp**.

Cohen, J. B., note on some double thiosulphates, 38.

Colman, H. G., and W. H. **Perkin**, jun., the synthetical formation of closed carbon-chains. Part II (*continued*). Some derivatives of tetramethylene, 228.

Cowper, R., obituary notice of, 473.

Cundall, J. T. See W. A. **Shenstone**.

D.

Deehan, M., note on an improved form of apparatus for the separation of iodine, bromine, and chlorine, 690.

Dingwall, J. See P. F. **Frankland**.

Divers, E., and T. **Haga**, reduction of nitrites to hydroxylamine by hydrogen sulphide, 48.

—— —— the relations between sulphites and nitrites of metals other than potassium, 659.

Dunstan, W. R., and T. S. **Dymond**, on the formation of hyponitrites, 616.

Dymond, T. S. See W. R. **Dunstan**.

Dyson, G., the action of salicylic aldehyde on sodium succinate in presence of acetic anhydride, 61.

E.

Evans, H. S., obituary notice of, 475.

F.

Fowler, G. J. See G. H. **Bailey**.

Frankland, P. F., and J. **Dingwall**, the decomposition of potassium chlorate and perchlorate by heat, 274.

Freer, P. C., and W. H. **Perkin**, jun., synthetical formation of closed carbon-chains. Part I (*continued*). The action of ethylene bromide on the sodium-derivatives of ethylic acetoacetate, benzoylacetate, and acetonedicarboxylate, 820.

G.

Gowland, W., and **Yoshima Koga**, on silver containing bismuth, 410.

Greenall, T. H. See T. E. Thorpe.

Griffiths, A. B., agricultural experiments with iron sulphate as a manure during 1886, 215.

H.

Haga, T., the effects of dilution and the presence of sodium salts and carbonic acid upon the titration of hydroxylamine by iodine, 794.

Haga, T. See also E. Divers.

Hall, J. A., some analogous phosphates, arsenates, and vanadates, 94.

—— some ethereal salts of the vanadium acids, 751.

Harden, A., on the action of silicon tetrachloride on the aromatic amido-compounds, 40.

Hartley, W. N., researches on the relation between the molecular structure of carbon compounds and their absorption-spectra. Part VIII. A study of coloured substances and dyes, 152.

—— spectroscopic notes on the carbohydrates and albuminoids from grain, 58.

Henderson, G. G., action of triphenylmethyl bromide on ethyl sodiomalonate, 224.

J.

James, J. W., on the formation of ethylic cyanacetoacetate, 287.

—— the action of chlorine on organic thiocyanates. Part I. Methyl thiocyanate, 268.

Japp, F. R., diphenylglyoxaline and methyldiphenylglyoxaline, 557.

Japp, F. R., and C. I. Burton, anhydracetonebenzil, 420.

—— —— condensation compounds of benzil with ketones, 431.

—— —— on some azines, 98.

Japp, F. R., and E. Cleminshaw, constitution of glycosine, 552.

Japp, F. R., and N. H. J. Miller, preparation and hydrolysis of hydrocyanides of the diketones, 29.

K.

Kimmins, C. W., periodates, 356.

Kinch, E., the amount of chlorine in rain-water collected at Cirencester, 92.

Koga, Yoshima. See W. Gowland.

L.

Laurie, A. P. See T. E. Thorpe.

Ling, A. R., isomeric change in the phenol series. I. The action of bromine on the dibromonitrophenols, 147.

—— isomeric change in the phenol series (Second Part), 782.

Lowe, C. W., dibenzyl ether, 700.

M.

McGowan, G., further notes on the dihaloid derivatives of thiocarbamide, 378.

sulphinic compounds of carbamide and thiocarbamide, 666.

Meldola, R., and F. W. Streatfeild, notes on anhydro-compounds. I. Ethenyltriamidonaphthalene, 691.

—— —— researches on the constitution of azo- and diazo-derivatives. I. Diazoamido-compounds, 102.

—— —— researches on the constitution of azo- and diazo-derivatives. II. Diazoamido-compounds, 134.

Mendeléef, D., the compounds of ethyl alcohol with water, 778.

Meyer, V., and A. W. Warrington, the action of acetyl chloride on acetoximes, 683.

Miller, A. K., notes on the recent papers by A. von Baeyer and J. Thomsen, "On the constitution of benzene," 208.

Miller, N. H. J. See F. R. Japp.

Morley, F. H., note on substitution in the benzene nucleus, 579.

Muir, M. M. P., and D. J. Carnegie, contributions from the laboratory of Gonville and Caius College, Cambridge. On bismuthates, 77.

N.

Nicol, W. W. J., supersaturation of salt solutions, 389.

P.

Perkin, W. H., sen., on tartaric and racemic acids and the magnetic rotation of their ethereal salts, 362.

—— on the magnetic rotation and densities of choral, chloral hydrate and hydrated aldehyde, 808.

Perkin, W. H., jun., dehydracetic acid, 484.

— synthetical formation of closed carbon-chains. Part I (*cont.*). Trimethylenedicarboxylic acid, 849.

— on the synthetical formation of closed carbon-chains. Part II. On some derivatives of tetramethylene, 1.

— the synthetical formation of closed carbon-chains. Part II (*cont.*). On the action of trimethylene bromide on the sodium compounds of ethylic acetoacetate, benzoylacetate, *p*-nitrobenzoylacetate, and acetone dicarboxylate, 702.

— the synthetical formation of closed carbon-chains. Part III. Some derivatives of pentamethylene, 240.

— See also H. G. **Colman**, P. C. **Freer**.

Pickering, S. U., decomposition of sodium carbonate by fusion, 72.

— the heat of hydration of salts. Cadmium chloride, 75.

— the influence of temperature on the heat of dissolution of salts, 290.

— on the thermal phenomena of neutralisation, and their bearing on the nature of solution and the theory of residual affinity, 593.

Purdie, T., the action of metallic alkylates on mixtures of ethereal salts with alcohols, 627.

R.

Ramsay, W., and S. **Young**, evaporation and dissociation. Part VII. A study of the thermal properties of a mixture of ethyl alcohol and ethyl oxide, 755.

Ramsay, W. See also H. C. **Reynolds**.

Rennie, E. H., phlorizin, 634.

— the colouring matter of *Drosera Whittakeri*, 371.

Reynolds, E. J., the composition of Prussian blue and Turnbull's blue, 644.

Reynolds, J. E., silicon compounds and their derivatives. I. Action of silicon tetrabromide on thiocarbamide, 202.

— researches on silicon compounds and their derivatives. II. A new chlorobromide of silicon, 590.

Reynolds, H. C., and W. **Ramsay**, experiments for comparing the equivalent of zinc with that of hydrogen, 854.

Richardson, A., action of heat on peroxide of nitrogen, 397.

— action of light on the hydrides of the halogens in presence of oxygen, 801.

Ridsdale, C. H. See J. E. **Stead**.

Romanis, R., certain products from teak, 868.

Ruhemann, S., formation of pyridine-derivatives from citric acid and on the constitution of pyridine, 403.

Ruhemann, S., and S. **Skinner**, anacardic acid, 663.

S.

Sear, F., obituary notice of, 477.

Shenstone, W. A., and J. T. **Cundall**, ozone from pure oxygen: its production and action on mercury with a note on the silent discharge of electricity, 610.

— — the volumetric relations of ozone and oxygen. A lecture experiment, 625.

Skinner, S. See S. **Ruhemann**.

Southby, E. R., obituary notice of, 476.

Stead, J. E., and C. H. **Ridsdale**, crystals in basic converter slag, 601.

Streatfeild, F. W. See R. **Meldola**.

T.

Teed, F. L., potassium chlorate of perchlorate, 283.

Thompson, C. See C. R. A. **Wright**.

Thomson, A. See T. **Carnelley**.

Thorpe, T. E., and T. H. **Greenall**, on morindin and morindon, 52.

Thorpe, T. E., and A. P. **Laurie**, on the atomic weight of gold, 565, 866.

Thorpe, T. E., and J. W. **Young**, on the atomic weight of silicon, 576.

Turner, T., influence of silicon on the properties of iron and steel. I, 129.

W.

Warington, R., a contribution to the study of well waters, 500.

— on the distribution of the nitrifying organism on the soil, 118.

Warrington, A. W. See V. **Meyer**.

Watson, H. W., obituary notice of, 477.

Weldon, W., obituary notice of, 480.

Werner, E. A., researches on chromorganic acids, 383.

Wright, C. R. A., and C. **Thompson**, note on a new class of voltaic combinations in which oxidisable metals are replaced by alterable solutions, 672.

Y.

Yoshida, H., on aluminium in th ashes of flowering plants, 718

Young, J. W. See T. E. Thorpe.

Young, S. See W. Ramsay.

INDEX OF SUBJECTS.

TRANSACTIONS. 1887.

A.

Absorption-spectra, relation between the molecular structure of carbon compounds and their. Part VIII, 152.
Acetates, ethereal, action of alcohols and metallic alkylates on, 632.
Acetobutyl alcohol, 718.
—— bromide, 726.
Acetopropyl alcohol, 829, 831
Acetoximes, action of acetyl chloride on, 683.
Acetyltrimethylene, magnetic rotation of, 832.
Acetyltrimethylenecarboxylic acid, action of water on, 829.
—— —— decomposition of, by heat, 831.
Acetyltrimethylenedicarboxylic acid, 847
"Acid-brown," description and measurement of the spectrum of, 198.
Affinity, residual, 593.
Agricultural experiments with iron sulphate as a manure, 215.
Albumin, absorption-spectrum of, 59.
Alcohols and ethereal salts, action of metallic alkylates on mixtures of, 627.
Aldehyde, hydrated, density and magnetic rotation of, 813.
Allylmalonic acid, 16.
Aluminium in the ashes of flowering plants, 718.
Amido-azo-α-naphthalene, description and measurement of the spectrum of, 190.
Amido-azo-β-naphthalene, description and measurement of the spectrum of, 191.
Amido-compounds, aromatic, action of silicon tetrachloride on, 40.
Amyl pyrovanadate, 754.
—— vanadate, 753.
Amylanhydracetonebenzil, 433.
Anacardic acid, 663
Anhydracetonebenzil, 120.
Anhydracetophenonebenzil, 429.
Anhydro-bases, notes on, 691.
Anilic acid, chlorobrom-, 781
Aniline, diazotised *m*-nitro-, action of, on *p*-nitraniline, 102
Annual General Meeting, March 30th, 1887, 452.
Arsenates, phosphates, and vanadates, analogous, 91.
Ash of flowering plants, aluminium in, 718.
Association, 782.
Atomic weights, determinations of, by means of the normal sulphate, 676.
Aurin, description and measurement of the spectrum of, 167.
Azines, 98.
Azo- and diazo-derivatives constitution of. II. Diazo-amido-compounds, 134.
—— —— —— researches on the constitution of, 102.
Azobenzene, description and measurement of the spectrum of, 176.

B.

Bacterium aceti, action of, on erythrol, 641.
—— —— action of, on glycerol, 689.
—— —— action of, on glycol, 638.
—— *xylinum*, note on the cellulose formed by, 613.
Balance Sheet of the Chemical Society from March 22nd, 1886, till March 21st, 1887, 467.
—— —— of the Research Fund from March 22nd, 1886, till March 21st, 1887, 468.
Barium chromoxalates, 388.
—— cuprous thiosulphate, 30.
Basic converter slag, crystals in, 601.

Beans, iron sulphate as a manure for, 219.
Benzene, constitution of, 208.
—— nucleus, substitution in the, 579.
Benzene-azo-β-naphtholsulphonic acid, measurement and description of the spectrum of, 196.
Benzenoid compounds, an explanation of the laws which govern substitution in, 258, 583.
Benzil, condensation products of, with ketones, 131.
—— dihydrocyanide, 29.
Benzoylbutyl alcohol, 733.
—— bromide, 732.
Benzoyltrimethylenecarboxylic acid, action of water on, 837.
Benzyl-*m*-nitraniline, 113.
Benzyl-*p* nitraniline, 113.
—— action of diazotised *m*-nitraniline on, 114.
Biebrich scarlet, description and measurement of the spectrum of, 194.
Bismarck brown, description and measurement of the spectrum of, 180.
Bismuthates, 77.
Bismuth sulphate, 679.
Bromanil, 118.
Bromine, iodine, and chlorine, improved form of apparatus for the separation of, 690.
—— liberation of, from hydrogen bromide by the action of light in presence of oxygen, 801.
Butyl vanadate, 753.

C.

Cadmium chloride, heat of hydration of, 75.
Calcium tetramethylenecarboxylate, distillation of, with lime, 229.
Cane-sugar, absorption spectrum of, 59.
Carbamide, sulphinic compounds of, 666.
—— trichloromethylsulphinate, 668.
Carbon, absorption of gases by, 249.
—— -chains, closed, synthetical formation of, 1, 228, 210, 702, 820, 819.
—— compounds relation between the molecular structure and their absorption spectra. Part VIII, 152.
—— reaction of absorbed oxygen on, at various temperatures, 252.
Casein, absorption-spectrum of, 59.
Cellulose formed by *Bacterium xylinum*, 643.
Chloral, density and magnetic rotation of, 808.
Chloral hydrate, density and magnetic rotation of, 809
Chlorine, bromine, and iodine, improved form of apparatus for the separation of, 690.
—— liberation of from hydrogen chloride by the action of light in presence of oxygen, 802.
Chrom-organic acids, 383.
Chromoxalates, 383.
Chrysoidine, description and measurement of the spectrum of, 178.
Citrazinamide, 106.
Citrazinic acid, 407.
Copper sulphate, influence of temperature on the heat of dissolution of, 321.
Croceine scarlet, description and measurement of the spectrum of, 195.
Cumene-azo-β-naphtholdisulphonic acid, description and measurement of the spectrum of, 187.
Cuprous barium thiosulphate, 39.
—— potassium thiosulphate, hydrated and anhydrous, 38.
Cyanuric chloride, best method for preparing, 269.

D.

Dehydracetic acid, 484.
—— —— bromo-, 490.
—— —— oxime of, 493.
Dehydracetonebenzil, 420.
Dextrose from phlorizin, 636.
Diacetyltetramethylenedicarboxylic acid, 26.
Diastase, absorption spectrum of, 60.
Diazoamidobenzene, *m*-dinitro-, 107.
—— *p*-dinitro-, 102.
Diazoamido-compounds, 102.
and their constitution, 484, 448.
dinitro-, decomposition by cold hydrochloric acid, 486.
Diazobenzene chlorides, decomposition of, by hydrochloric acid, 106.
Diazobenzylamidobenzene, *m*-dinitro-, 113.
—— *p*-dinitro-, 112.
Diazoethylamidobenzene, *m*-dinitro-, 108.
Diazotised metanitraniline, action of, on *p*-nitraniline, 102.
Dibenzyl ether, 700.
Dibenzylglycosine, 555.
Dicoumarin, preparation of, 62.
Didymium sulphate, 682.
Dihydrocoumaric acid and its salts, 68.
Dihydrocoumarin, 70.

Diisopropylacetoxime, and its behaviour with acetyl chloride, 684, 685.
Diketones, preparation and hydrolysis of hydrocyanides of, 29.
Dimethylanhydracetonebenzil, 432.
Diphenanthryleneazotide, 101.
Diphenylglyoxaline, 557.
Dipropyl acetoxime, 689.
action of acetic chloride on, 689.
Dissociation and evaporation, 755.
Dissolution of salts, heat of, influence of temperature on, 290.
—— theory of, 779.
Ditetramethylene ketone, 236.
Dithiocarbamide dibromide, 378.
—— dichloride, action of hydrogen sulphide and of cyanides on, 380.
—— di-trichloromethylsulphinate, 666.
Ditolueneazotide, 101.
Drosera Whittakeri, colouring matter of, 371.
Dyes and coloured substances, a study of, 152.

E.

Electricity, note on the silent discharge of, 622.
Erythrol, action of *Bacterium aceti* on, 641.
Ethenyltriamidonaphthalene and its derivatives, 691.
Ethereal salts and alcohols, action of metallic alkylates on mixtures of, 627.
Ethyl acetoacetate, action of ethylene bromide on the sodium-derivative of, 820.
action of trimethylene bromide on the sodium-derivative of, 702.
acetonedicarboxylate, action of ethylene bromide on the sodium-derivative of, 820, 845.
—— —— action of trimethylene bromide on the di-sodium-derivative of, 702, 739.
—— acetylcitrate, 404.
—— acetyltrimethylenecarboxylate. 825.
—— - action of phenylhydrazine on, 837.
- action of phosphoric chloride on, 841.
· oxidation of, 840.
acetyltrimethylenedicarboxylate, 845.
alcohol and ether, alteration of volume on mixing, 768, 774.
Ethyl alcohol and ether, thermal properties of a mixture of, 755.
—— —— the compounds of, with water, 778.
—— benzoylacetate, action of ethylene bromide on the sodium-derivative of, 820.
action of trimethylene bromide on the sodium-derivative of, 702, 726.
—— ω-bromethylacetoacetate, 833.
—— butane-$\omega_1\omega_2$-tetracarboxylate, 19.
—— chlorethylchlorocrotonate, 813.
—— cinnamate, conversion of, into methyl cinnamate, 628.
—— cyanacetoacetate, formation of, 287.
——· diacetoracemate, 369.
—— diacetotartrate, 368.
—— dichloracetoacetate, action of potassium cyanide on, 289.
disodiopentanetetracarboxylate, 243.
fumarate, conversion of, into methyl fumarate, 627.
—— hydric methyldehydrohexonedicarboxylate, 711.
—— methyldehydrohexonecarboxylate, 709.
—— —— action of bromine on, 725.
methyldehydrohexonedicarboxylate, 739.
p-nitrobenzoylacetate, action of trimethylene bromide on the sodium-derivative of, 702, 734.
—— *p*-nitrophenyldehydrohexonecarboxylate, 735.
—— orthovanadate, 752.
—— pentamethylenedicarboxylate, 214.
—— pentane-$\omega_1\omega_2$-tetracarboxylate, 211.
—— phenyldehydrohexonecarboxylate, 727.
· potassiocyanacetoacetate, 287.
· pyrovanadate, 751.
racemate, magnetic rotation of, 364.
—— sodiomalonate, action of triphenylmethyl bromide on, 224.
tartrate, magnetic rotation of, 363.
tetramethylenecarboxylate, 12.
—— tetramethylenedicarboxylate [1, 1]
2
· [1, 2], 23.
—— triphenylmethylmalonate, 225.
—— β-triphenylpropionate, 227.
Ethylanhydracetonebenzil, 432.
Ethylene bromide, action of, on the sodium-derivatives of ethyl acetoacetate, benzoylacetate, and acetonedicarboxylate, 820.

Ethylidene glycol, trichloro-, 813.
Ethyl-*m*-nitraniline, action of diazotised nitranilines on, 111.
Ethyl-*p*-nitraniline, action of diazotised nitranilines on, 110, 111.
Evaporation and dissociation, 755.

F.

"Fast-red," description and measurement of the spectrum of, 197.

G.

Gases, absorption of, by carbon, 249.
Gelatin, absorption-spectrum of, 59.
Glucose, absorption-spectrum of, 59.
Glycerol, action of *Bacterium aceti* on, 639.
Glycol, action of *Bacterium aceti* on, 638.
Glycosine, constitution of, 552.
Gold, atomic weight of, 565, 866.
Grain, spectroscopic notes on the carbohydrates and albuminoids from, 58.

H.

Halogens, hydrides of, action of light on, in presence of oxygen, 801.
Harpenden, well-waters of, 520.
Hay, meadow, iron sulphate as a manure for, 215.
Heat of dissolution of anhydrous sodium carbonate, 73.
—— —— of salts, influence of temperature on, 290.
—— of hydration of salts: cadmium chloride, 75.
—— thermal properties of a mixture of ethyl alcohol and ethyl oxide, 755.
Helianthin, description and measurement of the spectrum of, 102.
δ-Hexylene glycol, 722.
Hofmann's violet, description and measurement of the spectrum of, 171.
Hydrocoumaric acid, 70.
Hydrocoumarin, 71.
Hydrodicoumaric acid and its salts, 65.
Hydrodicoumarin, 66.
—— bromo-, 67.
Hydrogen, comparison of the equivalent of, with that of zinc, 854.
—— bromide, action of light on, in presence of oxygen, 804.
—— chloride, action of light on, in presence of oxygen, 801.
—— —— influence of liquid water in promoting the interaction between oxygen and, in presence of light, 806.
Hydrogen iodide, action of light on, in presence of oxygen, 805.
Hydroxydehydracetic acid and its acetyl-derivative, 491, 492.
Hydroxylamine, formation of, from silver, mercury, and sodium nitrites, 661.
—— reaction of, with ferrous hydroxide and water, 655.
—— titration of, by iodine, effects of dilution, and the presence of sodium salts and carbonic anhydride on, 794.
Hyponitrites, formation of, 616.

I.

Invertase, absorption-spectrum of, 60.
Iodine, bromine, and chlorine, improved form of apparatus for the separation of, 690.
—— liberation of, from hydrogen iodide by the action of light in presence of oxygen, 805.
"Iodine-green," description and measurement of the spectrum of, 174.
Iron, influence of silicon on the properties of, 129.
—— influence of silicon in, on its mechanical properties, 141.
—— specially pure, silicon in, 134.
—— sulphate, agricultural experiments with, as a manure, 215.
Isochoric lines, 773.
Isopropylamide of isobutyric acid, 688.

K.

Ketones, condensation compounds of benzil with, 481.

L.

Land, cropped, drainage water from, 513.
Light, action of, on the hydrides of the halogens in presence of oxygen, 801.

M.

Magnesium sulphate, 682.
—— —— influence of temperature on the heat of dissolution of, 320.
Magnetic rotation of chloral, chloral hydrate, and hydrated aldehyde, 808.

Maize starch, absorption-spectrum of, 59.
Mangel-wurzel, iron sulphate as a manure for, 217.
Methyl anacardate, 665.
—— dehydracetate, 496.
—— phenyllutidonecarboxylate, 498.
—— phosphate, 754.
—— tetramethylene ketone, 238.
—— thiocyanate, action of chlorine on, 268.
—— vanadate, 751.
Methylanhydracetonebenzil, 431.
Methyldehydrohexone, 723.
Methyldehydrohexonecarboxylic acid, action of water on, 717.
—— —— and its salts, 715.
Methyldehydrohexonedicarboxylic acid, 744.
—— —— action of water on, 747.
Methyldiphenylglyoxaline, 557.
Molecular structure of carbon compounds and their absorption-spectra, relation between. Part VIII, 152.
Morindin, 52.
Morindon, 52.
Murexide, description and measurement of the spectrum of, 199.

N.

α-β-Naphthazine, 99, 100.
Neutralisation, thermal phenomena of, 593.
Nitric nitrogen obtained from soils and sub-soils, 128, 129.
—— or nitrous acid produced in dilute urine with gypsum, seeded with soil from various fields, 120, 121, 122, 123.
—— oxide, reaction of, with ferrous hydroxide and water, 648.
Nitrification, order of priority of commencement of, in solutions seeded with soil of different depths, 125.
Nitrifying organism, distribution of the, in the soil, 118.
Nitrites and sulphites of metals other than potassium, reaction between, 650.
—— reduction of, to hydroxylamine by hydrogen sulphide, 48.
Nitrogen peroxide, action of heat on, 397.

O.

Obituary notices, 469.
Oxalates, ethereal, action of alcohols and metallic alkylates on, 629.
Oxygen, absorption of, by carbon, 252.
—— action of light on the hydrides of the halogens in presence of, 801.
—— and ozone, volumetric relations of, 625.
—— pure, preparation and storage of, 611.
Ozone and oxygen, volumetric relations of, 625.
—— from pure oxygen, 610.

P.

Pentamethylene-derivatives, 240.
Pentamethylenedicarboxylic acid, 244.
—— anhydride, 247.
Pentane-$\omega_2\omega_2$-tetracarboxylic acid, 242.
γ-Pentylene glycol, 836.
Periodates, 356.
Phenanthraquinone dihydrocyanide, 32.
Phenol, *o*-chloro-*p*-brom-*o*-nitro-, derivatives of, 791.
—— *p*-chlor-*o*-brom-*o*-nitro-, derivatives of, 788.
—— *p*-chloro-*p*-brom-*o*-nitro-, derivatives of, 790.
—— *p*-chlor-*o*-nitro-, action of bromine on, 787.
—— dichloro-*o*-nitro-, 782.
—— dichloro-*p*-nitro-, 786.
—— series, isomeric change in, 147, 782.
Phenols, dibromonitro-, action of bromine on, 147.
Phenyldehydrohexone, 731.
—— action of hydrogen bromide on, 732.
Phenyldehydrohexonecarboxylic acid, 728.
—— —— action of hydrogen bromide on, 732.
—— —— action of water on, 733.
—— —— *p*-nitro-, 736.
Phenylhydrazinedehydracetic acid, 494.
Phenyllutidone, 499.
Phlorizin, 634.
—— dextrose from, 636.
Phosphates, arsenates, and vanadates, analogous, 94.
Phosphorus, red, moist, action of light on hydrogen bromide and iodide in presence of, 806.
Pimelic acid, 242.
Plants, flowering, aluminium in the ashes of, 748.
Potassium aurobromide, preparation of pure, 868.
—— chlorate, decomposition of, by heat, 274, 283.

Potassium chloride, influence of temperature on the heat of dissolution of, 306.
—— chlorobromanilate, 785.
—— chromoxalates, 384.
—— cuprous thiosulphate, hydrated and anhydrous, 38.
—— nitrate, influence of temperature on the heat of dissolution of, 308.
—— perchlorate, decomposition of, by heat, 274, 285.
—— periodates, 357.
—— silver thiosulphate, 39.
—— sulphate, influence of temperature on the heat of dissolution of, 319.
Potatoes, iron sulphate as a manure for, 222.
Propyl vanadate, 753.
Prussian blue, composition of, 641.
Pyridine, constitution of, 409.
—— -derivatives, preparation from citric acid, 403.
—— siliconchloride, 47.

Q.

Quinol, chlorotribromo-, 784.
—— diacetylchlorotribromo-, 784.
Quinoline siliconchloride, 47.
Quinone, a, formed in the destructive distillation of teak, 870.
—— chlorotribromo-, 783.

R.

Racemic acid, 362.
Rain-water collected at Cirencester, amount of chlorine in, 92.
—— —— at Rothamsted, chlorine, sulphuric anhydride, and ammonia in, 501.
Resin from teak, 869.
Rochelle salt, influence of temperature on the heat of dissolution of, 317.
Rosaniline base, description and measurement of the spectrum of, 164.
—— hydrochloride, description and measurement of the spectrum of, 169.

S.

Salicylic aldehyde, action of, on sodium succinate in presence of acetic anhydride, 61.
Salt solutions, supersaturation of, 380.
Salts, influence of temperature on the heat of dissolution of, 290.
Serin, absorption-spectrum of, 59.
Silicon, atomic weight of, 576.
—— chlorobromide, a new, 590.
—— compounds and their derivatives, 202.
—— dichloro-, di-β-naphthyldiamide, 15.
—— —— diphenyldiamide, 40.
—— —— *o*-ditolyldiamide, 44.
—— —— dixylyldiamide, 44.
—— in iron, influence of, on the mechanical properties, 141.
—— in specially pure iron, 134.
—— influence of, on the properties of iron and steel. Part I, 129.
—— tetrabromide, action of, on thiocarbamide, 202.
Silver containing bismuth, 410.
—— hydrogen tartrate, 370.
—— periodates, 358.
—— potassium thiosulphate, 39.
—— suboxide, 416.
Slag, basic converter, crystals in, 601.
Sodium acetate, influence of temperature on the heat of dissolution of, 315.
—— arsenate, 95, 97.
—— carbonate, anhydrous, heat of dissolution of, 73.
decomposition of, by fusion, 72.
influence of temperature on the heat of dissolution of, 313.
—— chloride, influence of temperature on the heat of dissolution of, 308.
—— hyponitrite, reaction of, with ferrous hydroxide and water, 654.
—— —— reaction of with sodium amalgam and water, 654.
—— nitrate, reaction of, with ferrous hydroxide and water, 655.
—— nitrite, reaction of, with ferrous hydroxide and water, 651.
—— periodates, 357.
—— phosphate, 97.
—— vanadate, 96.
Soil, distribution of the nitrifying organism in the, 118.
Solution, nature of, 598.
Solutions, nature of, 779.
Steel, influence of silicon on the properties of, 129.
Strontium chloride, influence of temperature on the heat of dissolution of, 309.
—— nitrate, influence of temperature on the heat of dissolution of, 311.
Substitution, an explanation of the laws which govern, in benzenoid compounds, 258, 583.

Sugar from phlorizin, nature of, 636.
Sulphate, normal, determinations of atomic weights by means of, 676.
Sulphites and nitrites of metals other than potassium, reactions between, 659.
Sulphoxyleneazo-β-naphtholdisulphonic acid, description and measurement of the spectrum of, 188.
Supersaturation of salt solutions, 389.

T.

Tartaric acid, 362.
Teak, certain products from, 868.
—— destructive distillation of, 869.
—— resin, 869.
Tectone, 871.
Tetramethylene aldehyde, 238.
—— derivatives, 1, 228.
Tetramethylenecarboxylic acid, 8.
Tetramethylenedicarboxylic acid [1, 1] and its salts, 4.
—— —— [1, 2], 22.
—— anhydride, 25.
Tetramethylenetetracarboxylic acid [1, 1, 2, 2], 17, 21.
Tetraphenylazine, 101.
Tetraphenyleneazine, 101.
Tetraphenylglycosine, 553.
Thiocarbamide, action of cyanides on, 380.
—— action of excess of bromine on, 378.
—— action of silicon tetrabromide on, 202.
—— dihaloid derivatives of, 378.
—— sulphinic compounds of, 666.
—— trichloromethylsulphinate, 667.
Thiocarbonyl chloride, action of chlorine on, 272.
—— tetrachloride, action of chlorine on, 273.
—— —— action of, on alcohol, 274.
Thiocyanates, organic, action of chlorine on, 268.
Thiosulphates, double, 38.
Tolylbenzene, α-bromo-, 87.
—— derivatives of, 87.
—— α- and β-dibromo-, 89.
Tolylbenzoic acid, β-dibromo-, 90.
Trichloromethylsulphonyl thiocarbamide, 669.
Trihydroxymethylnaphthaquinone from *Drosera Whittakeri*, 373.
Trimethylene bromide, action of, on the sodium compounds of ethylic acetoacetate, benzoylacetate, *p*-nitrobenzoylacetate, and acetonedicarboxylate, 702.
—— iodide, 12.
Trimethylenedicarboxylic acid, 819.
Triphenylmethane, description and measurement of the spectrum of, 162.
Triphenylmethyl bromide, action of, on ethyl sodiomalonate, 224.
β-Triphenylpropionic acid and its salts, 226.
Tropaeolin O, description and measurement of the spectrum of, 182.
—— OOO, description and measurement of the spectrum of, 184.
Turnbull's blue, composition of, 644.

V.

Vanadates, organic, 751.
—— phosphates and arsenates, analogous, 94.
Voltaic combinations, new class of, in which oxidisable metals are replaced by alterable solutions, 672.

W.

Well-waters. See Waters, well-.
Water, liquid, influence of, in promoting the interaction of hydrogen chloride and oxygen on exposure to light, 806.
—— rain-, at Cirencester, amount of chlorine in, 92.
—— —— at Rothamsted, chlorine, sulphuric anhydride, and ammonia in, 501.
Waters, drainage, composition of, 506.
—— well-, a contribution to the study of, 500.

Z.

Zinc, comparison of the equivalent of, with that of hydrogen, 854.
—— sulphate, 681.

ERRATA.

VOL. LI.

Page	Line			
30	16	from top,	*for*	"on cooling, and" *read* "and, on cooling,"
100	2	„ bottom,	„	"275°" *read* "278°."
524	19	„ top	„	"1880" *read* "1886."
651	18 & 20	„ bottom,	„	"nitrite" *read* "nitrate."

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

IMPERIAL AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

1383/36